# Petrolog 4

## Manual

Version 4.2.2
June 2025

The latest version of Petrolog4 and this manual can be downloaded from the Petrolog4 homepage at:
https://www.petrologsoftware.com

Register for updates and new version alerts,
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Petrolog4 is developed and maintained by *Friendly Solutions*

Friendly Solutions

# Contents

## Technical requirements, installation, and licencing

Petrolog4 runs under Windows operating system (XP or higher). Screen resolution should be set to higher than 1400 x 1000 pixels.

The current release requires a computer with a 64-bit processor. If you require a 32-bit version of the software, please email support@petrologsoftware.com.

***Note:*** Correct display of the Main form of Petrolog4 (Fig. 1) may require that the 'Text size' option in Display settings is set to 100% (in earlier versions of Windows, this is the DPI setting that should be set to 'Normal size' at Display Properties/Settings/Advanced/General). To check/change this setting, go to the 'System' section of the Control Panel.

## Installation

To instal the software, download Petrolog4.zip file from the website (petrologsoftware.com) and unpack its content into a folder on your computer.

***Note:*** Petrolog4 would not work correctly if placed in a shared/managed folder, i.e., a folder that is administered by OneDrive, Dropbox, Google Drive, or other file sharing software. We suggest making a folder C:\Petrolog4 or C:\Programs\Petrolog4.

***Note:*** Your computer must be connected to the internet when you start Petrolog4 for the first time.

Start the program by double-clicking on Petrlog4.exe. When Petrolog4 starts for the first time, the Registration form will open requesting you to enter your Licence Key and User Key (Fig. 1).

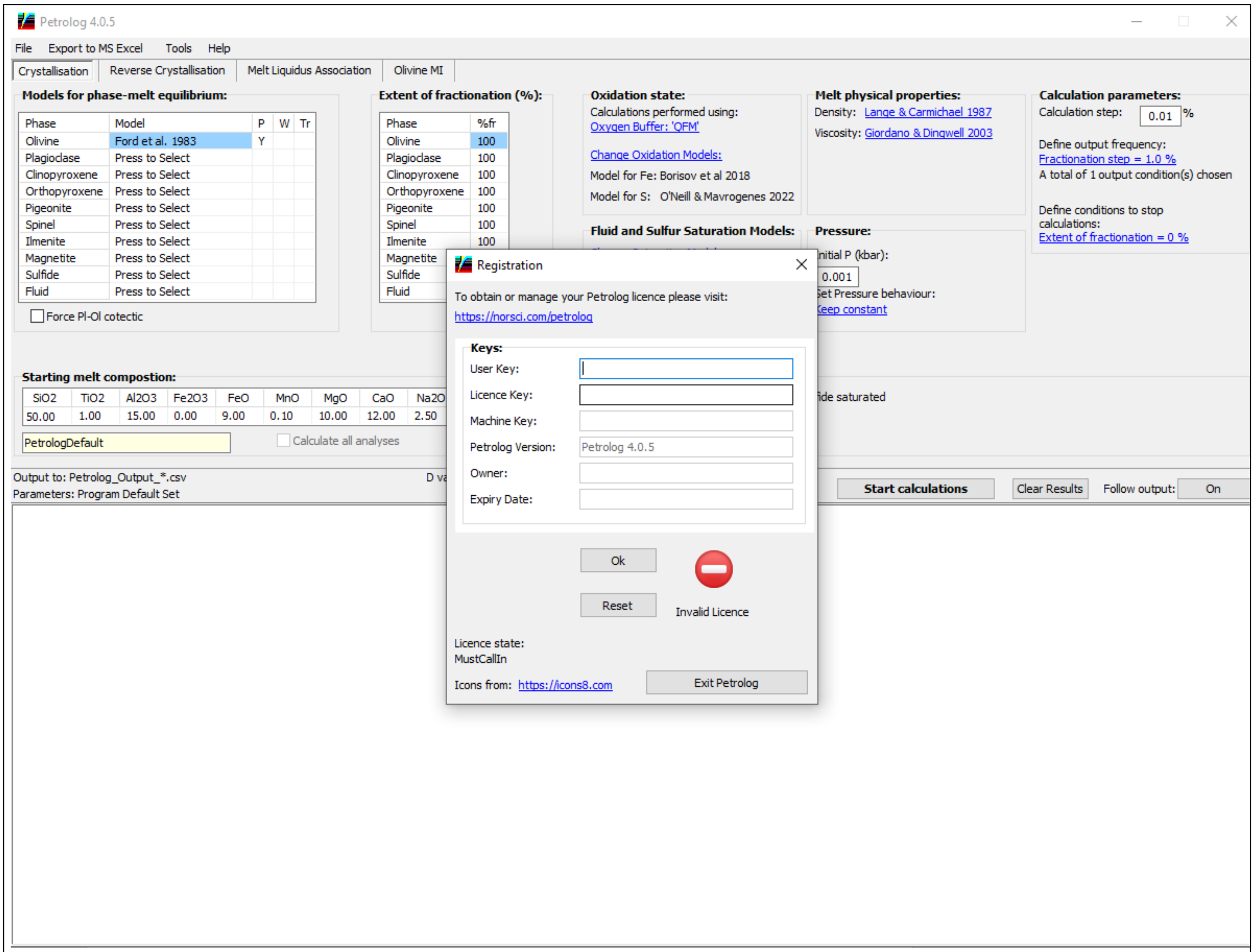



**Figure 1.** The Registration form of Petrolog4 before licence information is entered.

Once entered, click on the 'Ok' button to start using the software. Once licence is entered, you would not need to return to the Registration until the Licence Key expires. If you open the registration window, you will see your licence information (Fig. 2).

***Note:*** Do not move any individual files unpacked from Petrolog4.zip to other folders on your computer as this would result in a failure to start the program. If you would like to change the folder where Petrolog4 files are stored, copy all unpacked files to the new location.

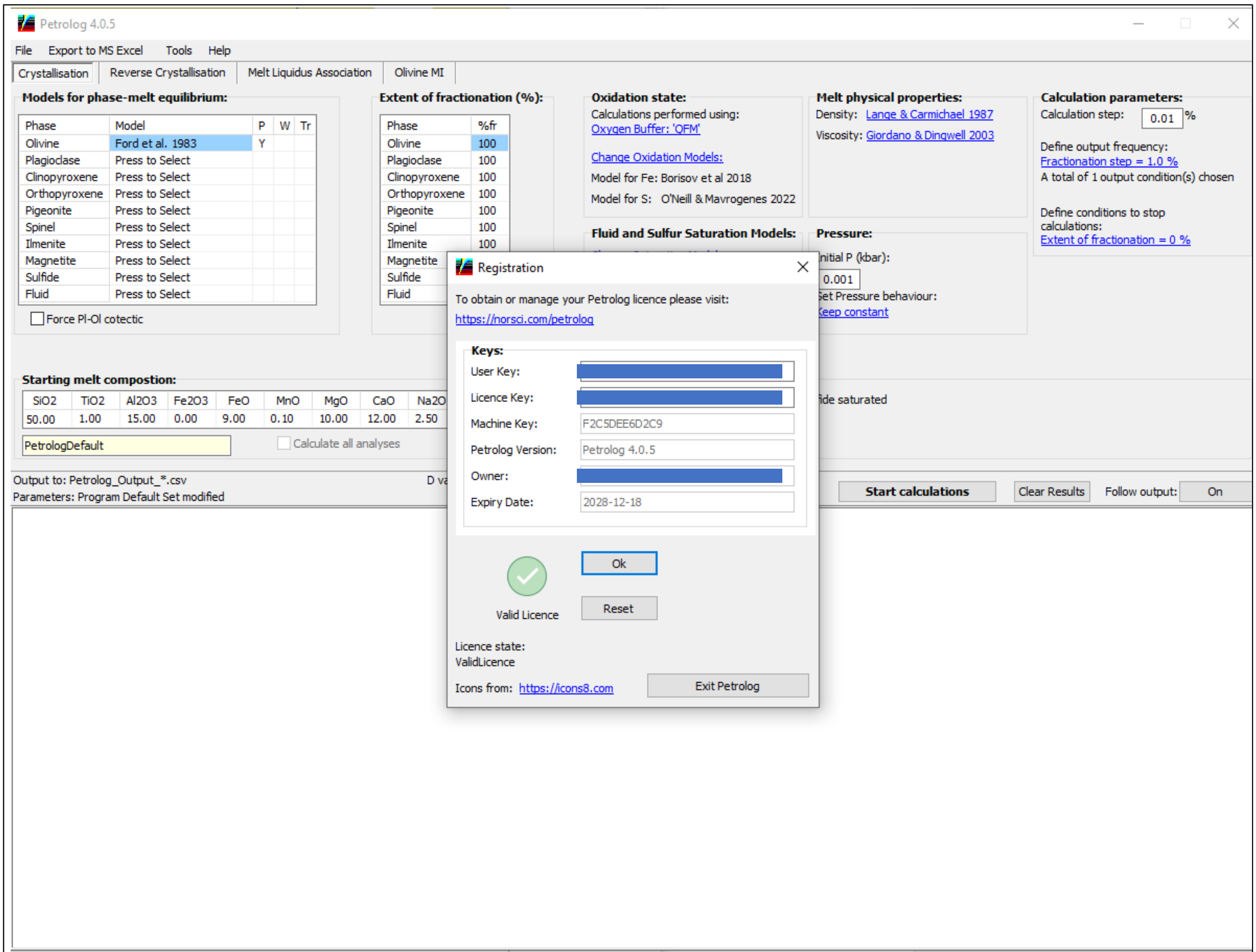



**Figure 2.** The Registration form of Petrolog4 after licence information is entered.

If you have not purchased your Keys before downloading the software, you can click on the link at the top left corner of the Registration form (https://norsci.com/petrolog) that will take you to the webpage where you can register and obtain the Keys.

To close the software without entering the Keys, click on the 'Exit Petrolog' button.

### *Possible issues when installing Petrolog4 under a non-English Windows installation*

In some cases, when starting Petrolog4 under a Windows installation that is not using English as the preferred language, an error may occur when the main form of the program is being generated (Fig. 3). In this case, please change the Windows preferred language to English. To do this, open Windows Settings and go to the 'Time and language' section.

Additionally, on such Windows installations another error may occur when Petrolog4 connects to the internet to check the validity of the licence (Fig. 4). In this case, please change the setting for the language that is used for non-Unicode applications (Fig. 5). To do this, open Windows Settings and go to the 'Time and language' section. Under the 'Language and region' subsection, open 'Region / Regional format' and set the language as shown on Figure 5.

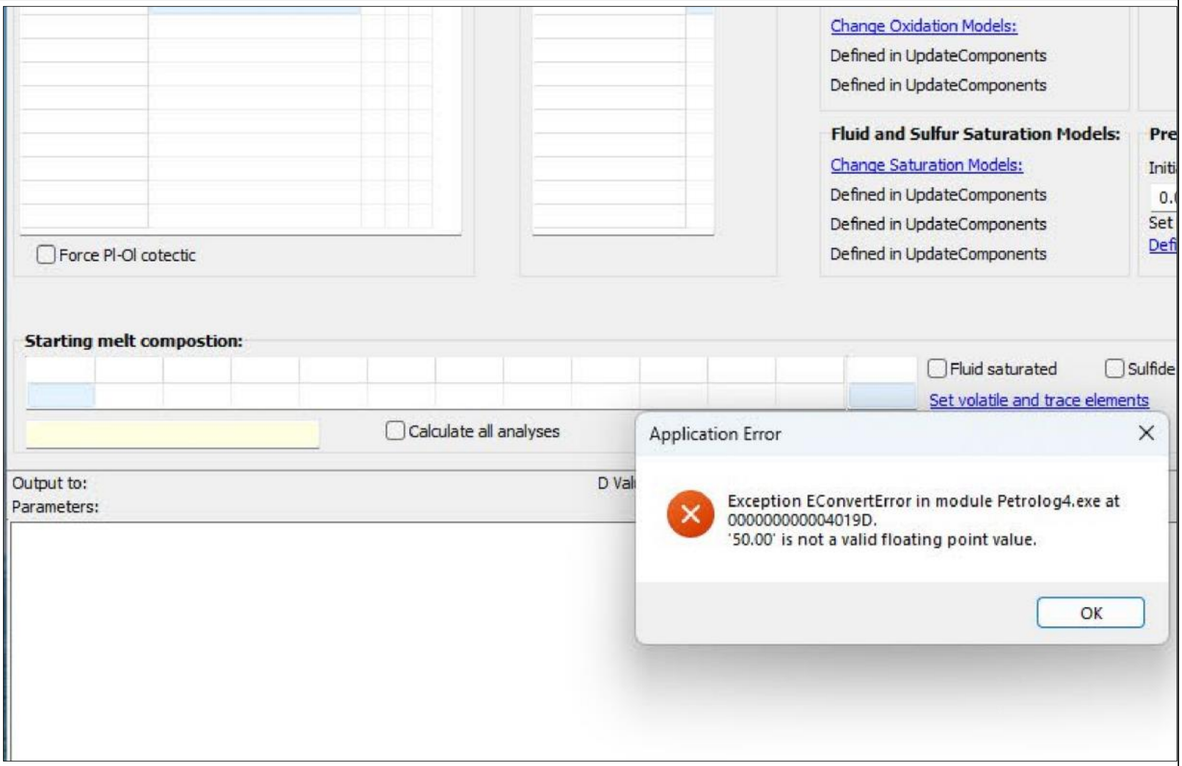



**Figure 3.** An error that may occur when starting Petrolog4 under a Windows installation that is not using English as the preferred language.

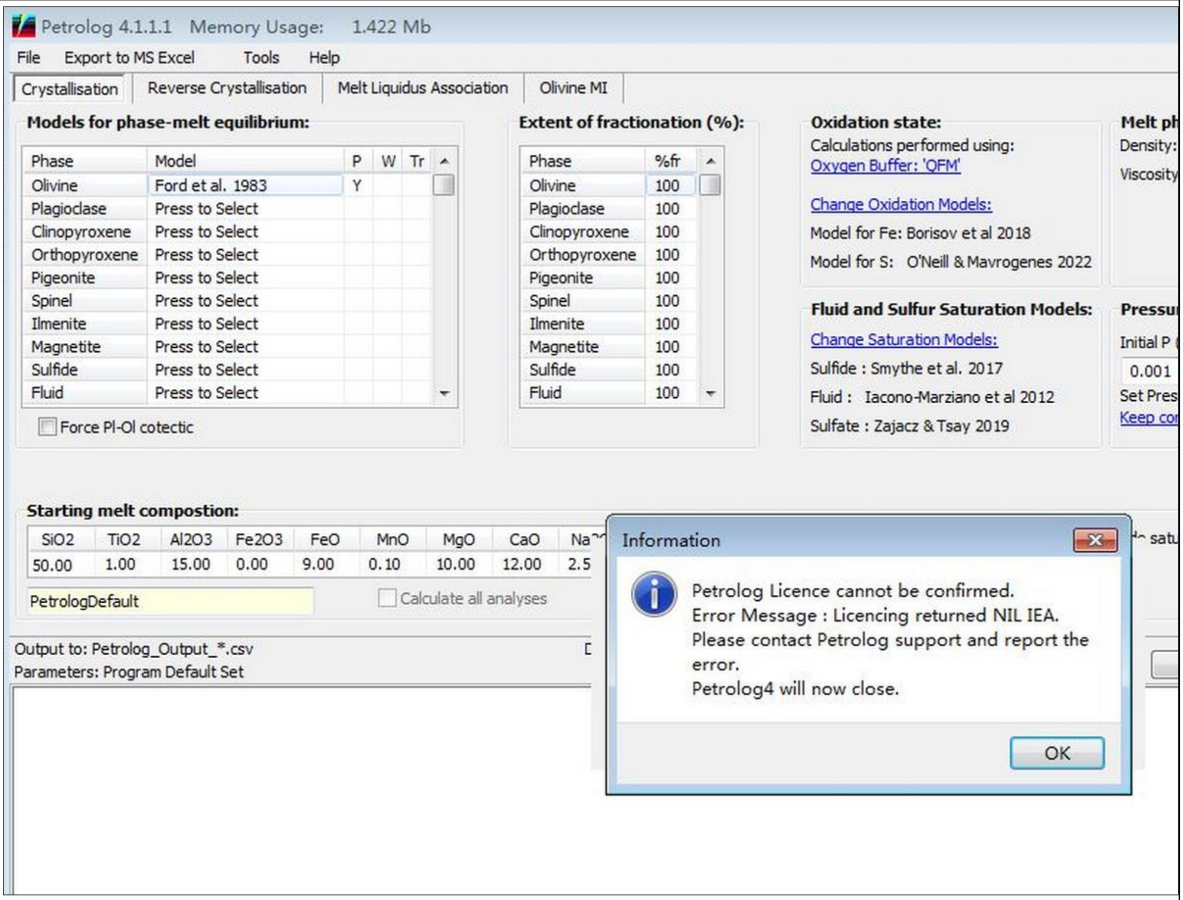



**Figure 4.** An error that may occur when opening the registration form under a Windows installation that is not using English as the preferred language.

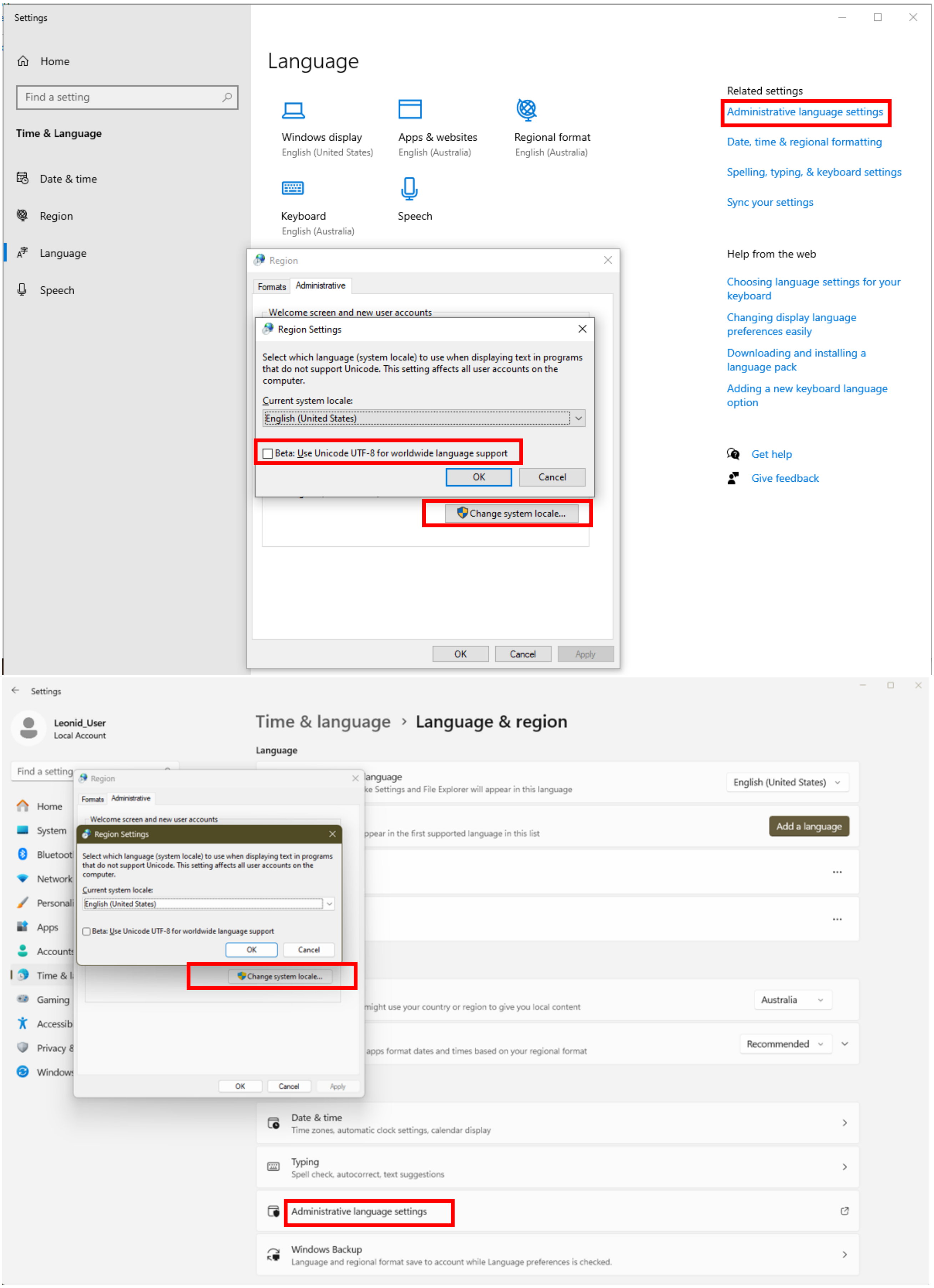



**Figure 5.** Windows Settings interface showing the 'Language; (Windows 10) or 'Language and region' (Windows 11) subsections of the 'Time and language' section (upper image - Windows 10, lower image Windows 11). For some Windows installations that are not using English as the preferred language, it may be required to change the setting for the language that is used for non-Unicode applications to English in the 'Administrative language settings' subsection. Ensure that the Beta tick-box is not ticked.

## Licencing

Petrolog4 licences can be purchased for a minimum of 1 year. A single licence can include several installations (licence allocations). The cost of the licence is determined by the number of years it covers and the number of installations it includes. One installation for one year costs AUD$100 in 2025.

Each Petrolog4 installation is linked to the computer the software is installed on, and the user who installed the software on that computer. More details are provided on https://norsci.com/?p=user-licences.

Every time Petrolog4 is started, the program will attempt to connect to the server and validate the licence. If Petrolog4 starts when the computer is off-line, this installation enters an off-line grace period. Each Petrolog4 licence allocation allows for a 30-day off-line grace period that is counted from the time the program last started when the computer it is installed on was online.

***Note:*** If Petrolog4 have not been run for over 30 days, it will not work if the computer is off-line when the program starts.

Each licence has a 14-day expiration date grace period. If the licence is not renewed within 14 days, Petrolog4 will stop working.

### *Moving Petrolog4 licence allocations to a different computer or a different user on the same computer*

If you have purchased a licence with a single allocation and would like to change the computer/user you use to run Petrolog4, you would need to logon to your account on norsci.com and deactivate the previous allocation. After that, you will be able to register your available allocation on a different computer and/or under a different user.

## 1. Overview of Petrolog4

Petrolog4 is software for modelling fractional and equilibrium crystallisation of silicate magmas at variable pressure, melt oxidation state and melt volatile contents.

Other calculation options include modelling reverse of fractional crystallisation and modelling post-entrapment re-equilibration of melt inclusions in olivine.

Modelling of crystallisation in Petrolog4 is based on the concept of pseudo-liquidus temperatures (Nathan, Vankirk, 1978; Nielsen, Dungan, 1983; Ariskin et al., 1986). The method relies on the ability of the mineral-melt equilibrium models to calculate liquidus temperature not only for the range of melt compositions where the minerals are stable, but also for melt compositions outside the stability regions of each mineral (i.e., pseudo-liquidus temperatures).

The essence of the technique is to compare calculated pseudo-liquidus temperatures for a selected set of mineral species that may crystallize from a given melt composition. The mineral with the highest calculated temperature is considered the mineral on the liquidus of the given melt composition. This mineral is subtracted from melt, and then the process is repeated. The algorithm automatically determines the order of appearance of phases on the liquidus of the melt.

***Note:*** Mineral-melt equilibrium models that can be included in Petrolog4 must calculate, at given values of pressure and oxygen fugacity, both the temperature at which the mineral appears on the liquidus of a given melt composition, and the composition of the mineral.

Minerals for which models meeting the above requirement are available in the current version are:
olivine; plagioclase; clinopyroxene; orthopyroxene; pigeonite; spinel; magnetite; ilmenite; quartz; orthoclase; nepheline and leucite.

Additionally, Petrolog4 includes other phases for which phase-melt equilibrium models require that the temperature of the melt is independently known. Thus, including such phases in calculations requires that the liquidus temperature of the melt is established using appropriate mineral-melt equilibrium models described above.

***Note:*** Phase-melt equilibrium models that can be included in Petrolog4 must calculate the composition of the phase at given values of pressure, temperature and oxygen fugacity.

Phases for which models meeting the above requirement are available in the current version are: immiscible sulphide melt; $H_2O$-$CO_2$ fluid, sulphate, apatite and zircon.

Compositions of all phases during calculations are fully mass- and charge-balanced for all elements including O. This allows for maintaining redox equilibrium between silicate melt, sulphide melt and $H_2O$-$CO_2$ fluid using available models of melt oxidation state as a function of pressure, temperature and oxygen fugacity. In the current version, such models are available for Fe and S, and thus these are the only elements that can have variable charges ($Fe^{2}$+ and $Fe^{3+}$ for Fe, $S^{2-}$ and $S^{6+}$ for S (note: oxidised S is $S^{4+}$ when present in the fluid phase). Atomic weights, element charges and redox equilibria used in Petrolog4 are listed in Appendix 1.

Petrolog4 subdivides elements into three groups: major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P and Cr), volatile elements (H, C, S, Cl, O) and trace elements (B, Be, Sc, V, Co , Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ru, Rd, Pd, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Re, Os, Ir, Pt, Pb, Th, U). During calculations, compositions of all phases can be displayed either as elemental concentrations or compound concentrations. Compound concentrations (either oxides or sulphides) are displayed for major and volatile elements only (see Section **2** for more details). Trace elements are always displayed using elemental concentrations.

Petrolog4 offers a model-independent algorithm (Danyushevsky, Plechov, 2011), which can incorporate a potentially unlimited number of phase-melt equilibrium models for major, volatile and trace elements; of solubility models in silicate melts for reduced and oxidised sulphur, fluid components and other elements; of melt oxidation state models; of models describing melt physical parameters such as density and viscosity; and other types of models. Currently available models are listed in Appendix 1.

### *1.1. Petrolog4 User Interface*

Petrolog4 can be used to perform four general types of calculations:

- Modelling Crystallisation,
- Modelling Reverse of Fractional Crystallisation,
- Estimation of Melt Liquidus Association, and
- Modelling Melt Inclusions in Olivine.

Each calculation type can be selected by choosing the appropriate tab on the Main form of the software (Figure 1.1). Four tabs corresponding to the four calculation types above are called ‘Crystallisation’, ‘Reverse Crystallisation’, ‘Melt Liquidus Association’ and ‘Olivine MI’.

Each tab window has three main parts: the top part (grey background) is used for setting the calculation parameters (Parameters Section); the middle part (white background) is used for recording calculation results (Output Section); and the optional bottom part (grey background) is used for recording non-critical debugging messages and warnings (Debug Section).

The Parameters Section has several entry fields and text boxes with white background (e.g., ‘Calculation step’ or ‘Initial pressure’), in which parameter values can be typed in, and several settings in blue, which can be changed by clicking on them and choosing a different setting in a pop-up window.

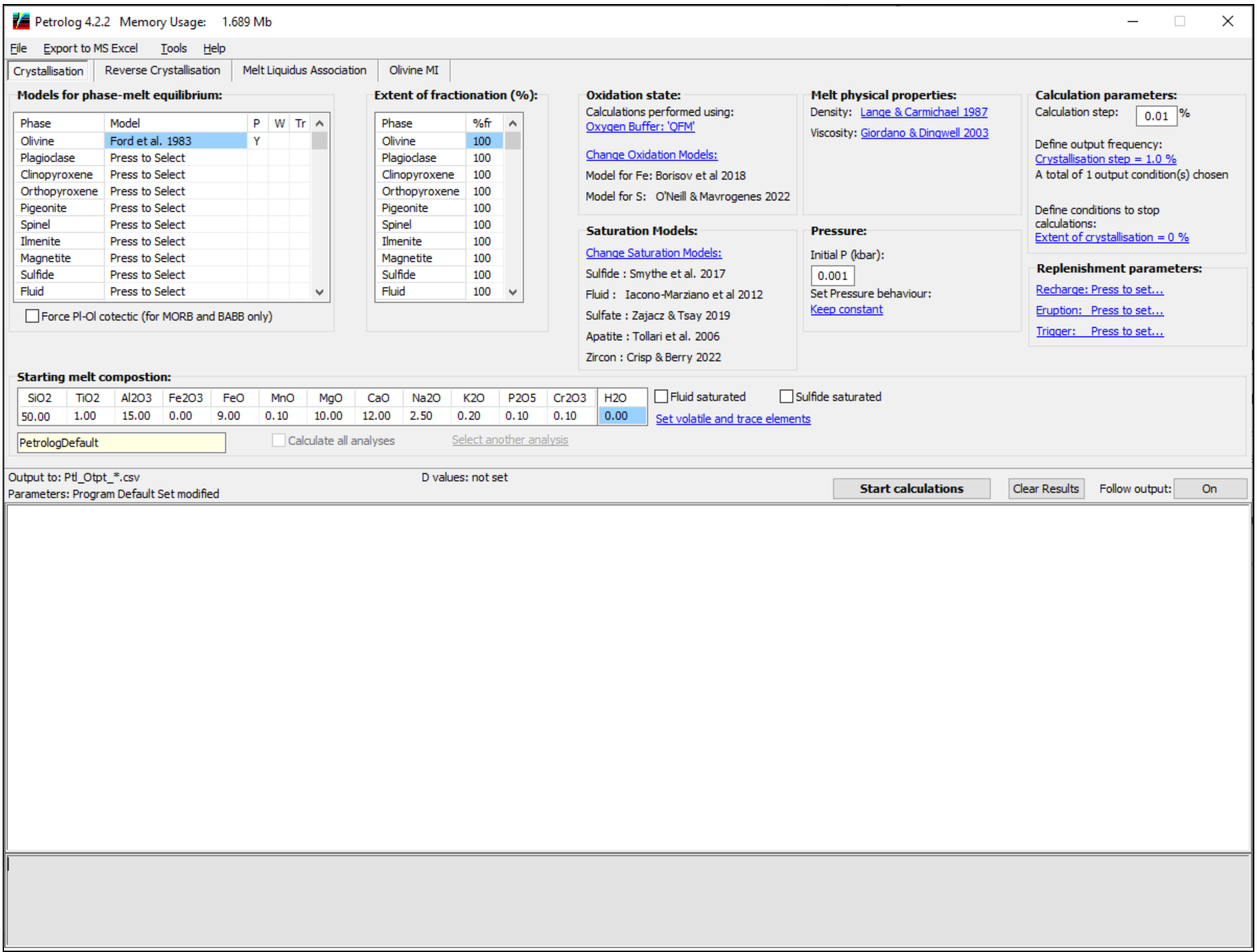



**Figure 1.1** ‘Crystallisation’ tab of Petrolog4 interface with the Default set of parameters loaded.

When parameters are set, calculations are started by pressing the ‘Start Calculations’ button at the right-hand corner of the Parameters Section. The Output Section will list the set of parameters chosen for calculation and calculation results. Text in the Output Section can be highlighted and copied by simultaneously pressing ‘Ctrl’ and ‘C’, and then pasted into a text editor. (see Section **2** for details), When calculation starts, the ‘Start Calculations’ button changes to the ‘Interrupt Calculations’ button, which can be used to abort the current run.

The program is loaded with the Program Default Set of parameters and a default starting composition (‘PetrologDefault’) and thus pressing the ‘Start Calculations’ button straight after the program is loaded would result in a default calculation.

Petrolog4.zip contains several recommended predefined sets of parameters for modelling crystallisation of several major geodynamic types of magmas such as mid-ocean ridge basalts and subduction-related magmas. These sets of parameters can also be downloaded from the Petrolog4 website.

***Note:*** It is possible to save a set of parameters as the Default Set that would be loaded automatically every time Petrolog4 starts (see Section 4.2.1 of this manual).

### *1.2. Petrolog4 Options*

Petrolog4 options control some aspects of data input and output and allow the user to choose several other high-level options of program behaviour. Petrolog4 Options form is opened by selecting the ‘Options’ item in the ‘Tools’ section of the Main Menu (Figs. 1.2 and 1.3).

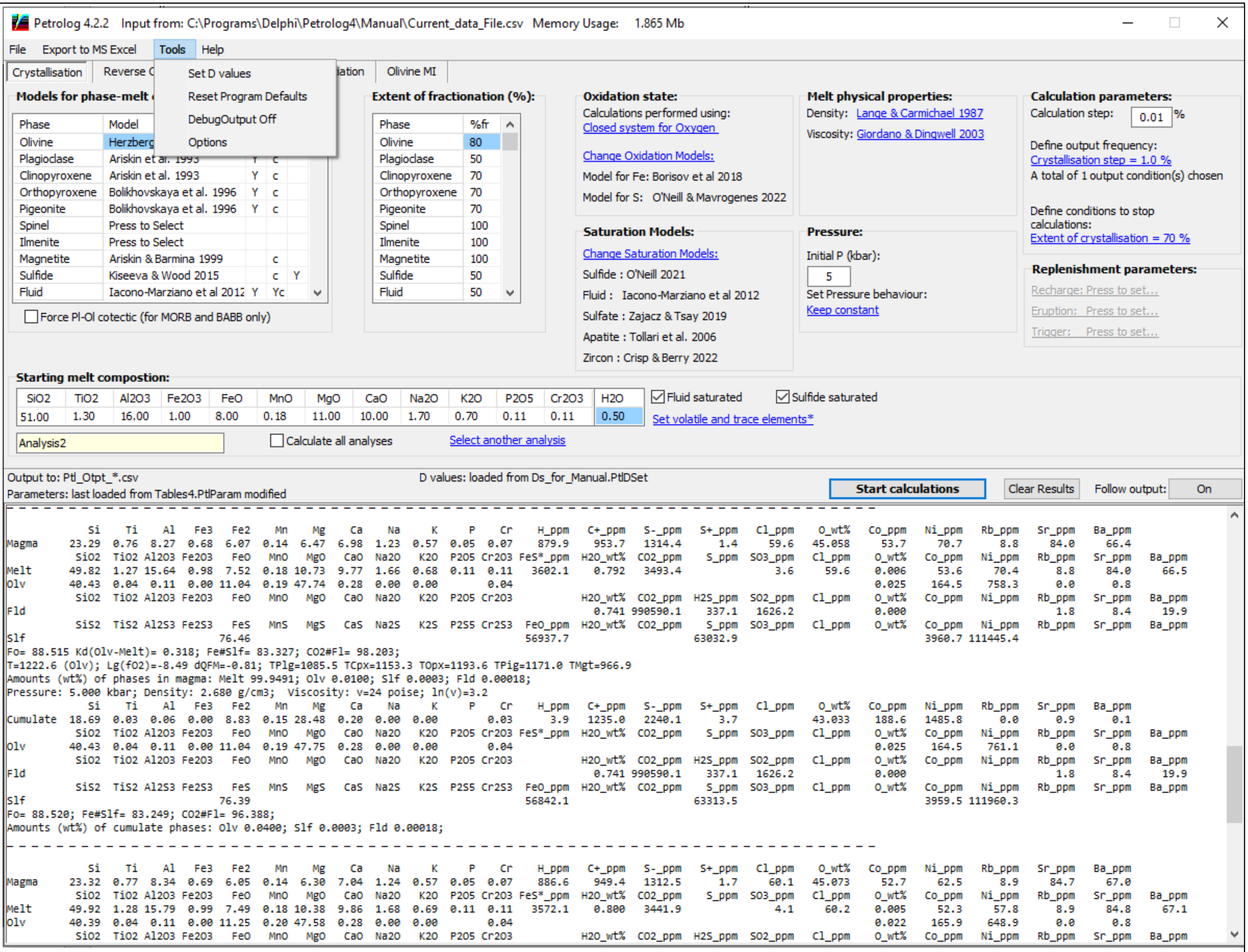


**Figure 1.2.** The main form of Petrolog4 with the content of the Tools Menu shown. Note that the Debug Section at the bottom of the Main Form is not displayed on this example as Debug output has been switched off by using the ‘DebugOutput On/Off’ item in the ‘Tools’ section of the Main Menu.

***Note:*** Petrolog4 options are different from calculation parameters that control how modelling is performed (see Section 4 for a detailed description of calculation parameters).

- ‘Save Data File Name with Parameters’ option defines whether a file with data (i.e., the starting compositions for calculations) is saved together with other calculation parameters (see Section **4.2**). Default value is ‘No’.

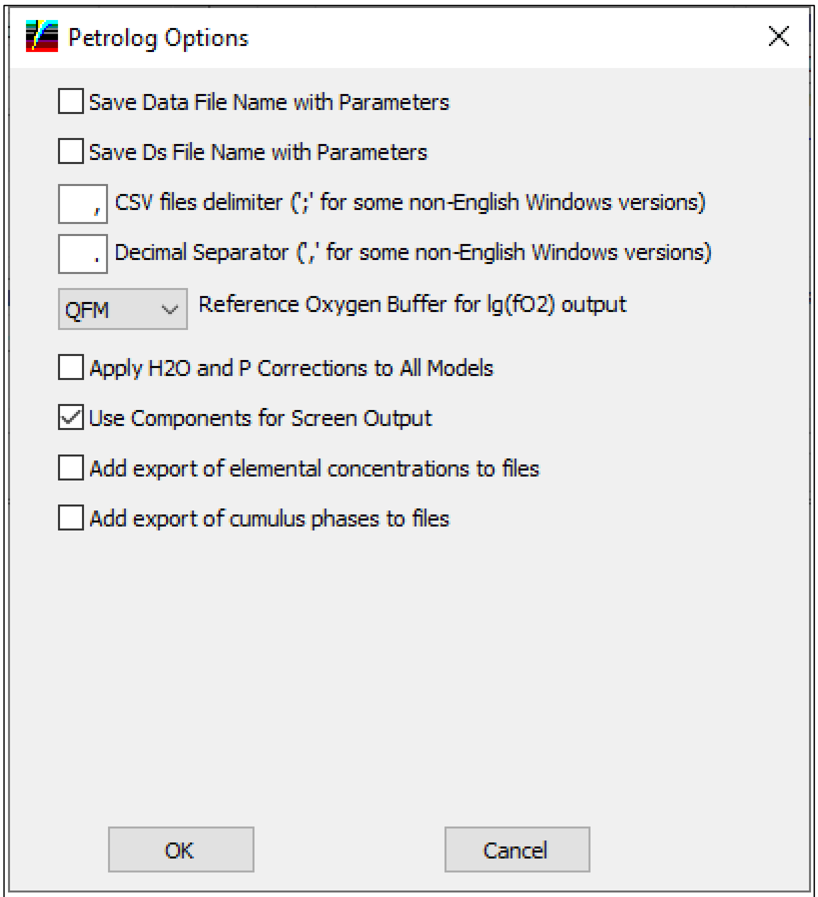



**Figure 1.3.** Petrolog4 Options form.

- 'Save Ds File Name with Parameters' option defines whether a file a user-defined set of distribution coefficients (D) for trace and volatile elements is saved together with other calculation parameters (see Sections 3 and 4.2). Default value is 'No'.

- 'CSV files delimiter' option defines how Petrolog4 saves the results of calculation to files (see Section 2.3). Default value is ','.

- 'Decimal Separator' option defines how Petrolog4 saves the results of calculation to files (see Section 2.3). Default value is '.'.

- 'Reference Oxygen Buffer for lg(FO2) output' option defines how Petrolog4 saves the results of calculation to files (see Section 4.1.8). Default value is 'QFM'.

- 'Apply H2O and P Corrections to All Models' option defines whether the user-defined corrections to the calculated pseudo-liquidus temperatures for the effects of melt $H_2O$ content and pressure are applied to mineral-melt equilibrium models that incorporate such effects. (see Sections 4.1.1.3 and 4.1.1.4). Default value is 'No'.

- 'Use Components for Screen Output' option defines whether concentrations of major and volatile elements are displayed using oxide or sulphide components or elements. (see Section 4.1.8). Default value is 'Yes'.

- 'Add export of elemental concentrations to files' option defines whether calculation output includes files with elemental concentrations in addition to files with component concentration (see Sections 2.2 and 4.1.8). Default value is 'No'.

- 'Add export of cumulus phases to files' option defines whether calculation output includes files with compositions of cumulus phases in addition to the combined composition of all cumulus phases (see Sections 2.2 and 4.1.8). Default value is 'No'.

# 2. Data Input and Output

## *2.1. Defining the Starting melt composition for calculations*

The starting composition is set in the 'Starting Melt Composition' subsection of the Parameters Section (Fig. 1.1). Petrolog4 allows for the starting composition(s) to be entered manually or loaded from a file.

### 2.1.1. Manual entry of the starting composition.

When the program is loaded, the 'Starting melt composition' subsection of the Parameters Section contains the default starting composition 'PetrologDefault'. This composition can be edited directly within this section. The concentrations of major elements and $H_2O$ are in wt.% oxides.

Trace and volatile element contents are set and/or edited by clicking on 'Set volatile and trace elements' label, which opens the 'Volatile and Trace Elements' pop-up window (Fig 2.1).

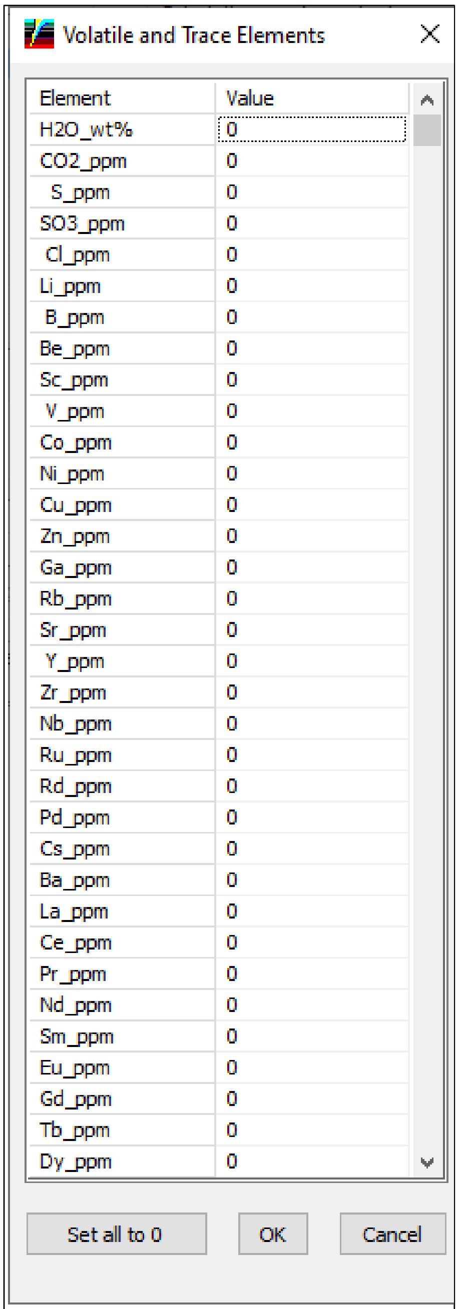



**Figure 2.1.** Window for setting volatile and trace element contents.

The concentrations of volatile and trace elements of interest are entered into the column 'Value' in wt. ppm (all but $H_2O$). All elements that have concentrations above zero will be included in calculations. To reset all concentration values to zero press 'Set all to 0' button. Pressing the 'Cancel' button will close the form without applying any changes that were made.

***Note:*** Sulphur can be entered as S or SO3 or both. When multiple forms of S are present in the starting composition, the total elemental S content is calculated by summing sulphur entered in different forms. The oxidation state of sulphur is determined during calculations based on the magma oxidation state (see Section 4.1.5). Reduced $S^{2-}$ is coupled to $Fe^{2+}$ in the melt.

***Note:*** If concentrations of at least one volatile or trace element are set to a non-0 value, a star ('*') appears next to the 'Set volatile and trace elements' label in the 'Starting melt composition' subsection.

### 2.1.2. Loading starting composition(s) from file.

The starting composition(s) can also be loaded from a file by using the 'Open data file' option in the 'File' menu (Fig. 2.2).

***Note:*** When a file is loaded, its name and full path are displayed at the top of the Petrolog4 Main form (Fig. 2.2).

The data file should contain analyses stored as rows with the first row containing element names. The program can read delimited text files that use 'tabs', blank spaces, commas or semicolons as delimiters. The recognised extensions for file names are '.txt', '.dat' and '.csv'.

***Note:*** The order of elements in the file is not prescribed. Petrolog4 identifies elements by analysing the first row of the data file.

The following abbreviations should be used (not case sensitive): SiO2, TiO2, Al2O3, Fe2O3, FeO, FeO* or FeOt, MnO, MgO, CaO, Na2O, K2O, P2O5, Cr2O3, H2O, CO2, S, SO2, SO3, Cl, B, Be, Sc, V, Co , Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ru, Rd, Pd, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Re, Os, Ir, Pt, Pb, Th, U. Concentrations of major element oxides and $H_2O$ should be supplied in wt.% and for all other elements in wt. ppm. Names of all elements supplied as wt. ppm can be followed by '_ppm'; the name for $H_2O$ can be followed by '_wt%'. Petrolog4 can also read melt compositions from its output files (section 2.2). At least 4 major elements $SiO_2$, FeO or $Fe_2O_3$, MgO and CaO must be present at above 0 concentrations to make a valid data file. The column containing analysis identifiers can be called either 'Name' or 'Sample' or 'Number' or 'Analysis'.

***Note:*** The data file can also contain other columns as described later in this manual (Sections 4.1.3 and 4.1.10).

***Note:*** When both FeO and the total Fe as FeO (FeO* or FeOt) columns are present in the file, the user will be asked to choose whether to load data from the Fe2O3 and FeO columns and ignore the total Fe values, or to load the total Fe as FeO and ignore the FeO and $Fe_2O_3$ values.

***Note:*** Sulphur can be entered as either S, or SO2, or SO3 in any combination. When multiple forms of S are present in the starting composition, the total elemental S content is calculated by summing sulphur entered in different forms. The oxidation state of sulphur is determined during calculations based on the magma oxidation state (see Section 4.1.5). Reduced $S^{2-}$ is coupled to $Fe^{2+}$ in the melt.

***Note:*** The starting composition in the 'Starting melt composition' subsection of the Main form does not change during calculations and can be used in subsequent calculations if required.

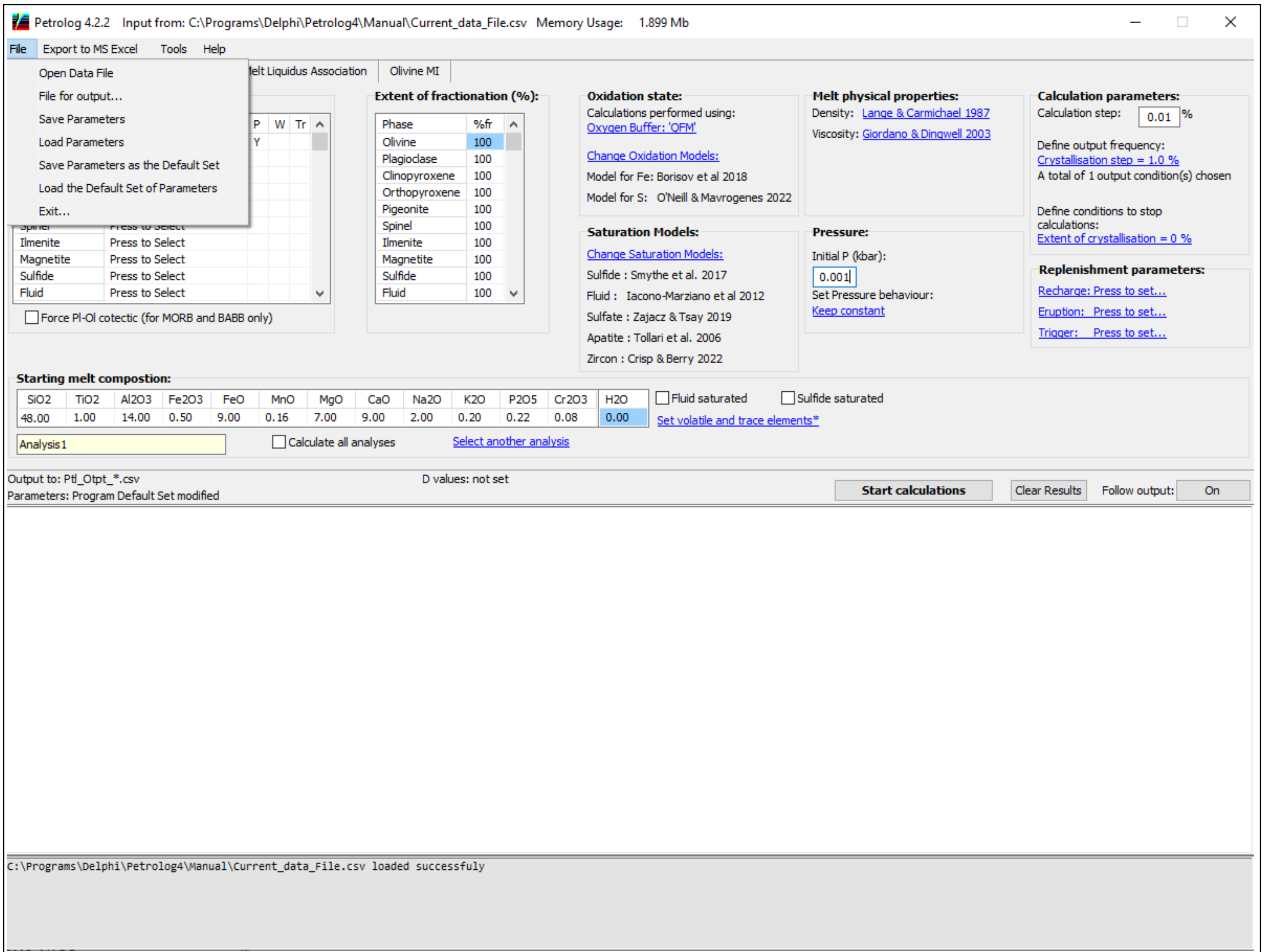
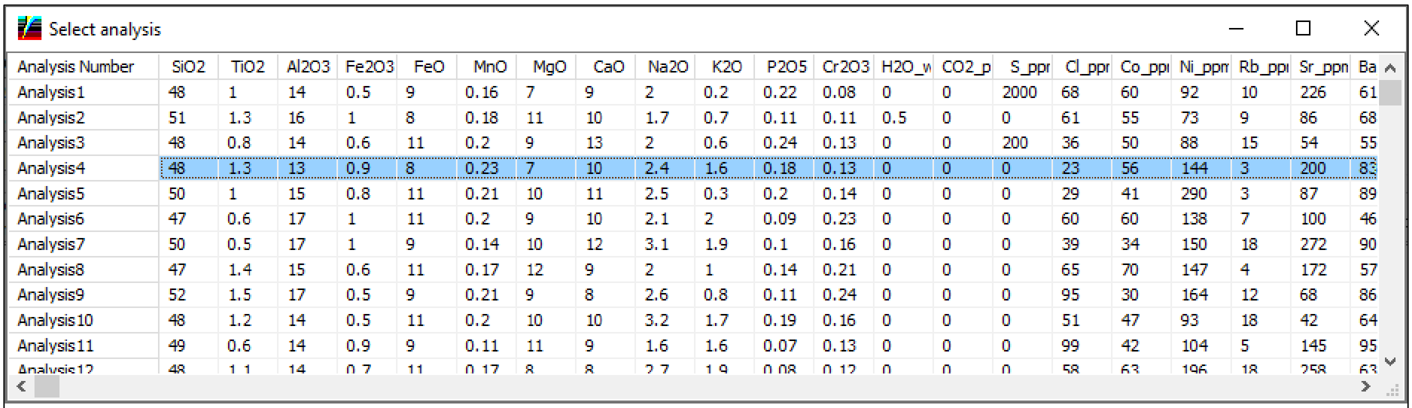



**Figure 2.2.** The Main form of Petrolog4 with the content of the File Menu shown. The name of the loaded data file with the starting compositions is displayed at the top of the form. The name of the loaded file with calculations parameters (if loaded) is displayed above the Output window on the left side of the form. The name of the file with distribution coefficients for trace and volatile elements (D values), if loaded, is displayed above the Output window in the centre of the form. The name of the file for saving the result is displayed above the Output window on the left side of the form.

When a file is loaded, the first analysis in the file is displayed in the 'Starting melt composition' subsection. The values in this analysis can be edited in Petrolog4 without affecting the data file stored on disk. When the

‘Start calculations’ button is pressed, the calculations will start using the composition displayed in the ‘Starting melt composition’ subsection.

If the data file contains more than one analysis, it is possible to choose another analysis by clicking on the ‘Select another analysis’ label in the ‘Starting melt composition’ subsection. In the pop-up window that appears (Fig. 2.3), <u>*double-click*</u> on the required analysis to choose it (click anywhere on the concentration values, not on the ‘Analysis Number’ column). This will close the window and return to the Main form. The concentration values for the chosen analysis will appear in the ‘Starting melt composition’ subsection of the Main form. To close the ‘Select analysis’ window without choosing an analysis, click on the cross in the top right corner.




| Analysis Number | SiO2 | TiO2 | Al2O3 | Fe2O3 | FeO | MnO | MgO | CaO | Na2O | K2O | P2O5 | Cr2O3 | H2O_w | CO2_p | S_ppr | Cl_ppr | Co_ppi | Ni_ppm | Rb_ppi | Sr_ppn | Ba |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Analysis1 | 48 | 1 | 14 | 0.5 | 9 | 0.16 | 7 | 9 | 2 | 0.2 | 0.22 | 0.08 | 0 | 0 | 2000 | 68 | 60 | 92 | 10 | 226 | 61 |
| Analysis2 | 51 | 1.3 | 16 | 1 | 8 | 0.18 | 11 | 10 | 1.7 | 0.7 | 0.11 | 0.11 | 0.5 | 0 | 0 | 61 | 55 | 73 | 9 | 86 | 68 |
| Analysis3 | 48 | 0.8 | 14 | 0.6 | 11 | 0.2 | 9 | 13 | 2 | 0.6 | 0.24 | 0.13 | 0 | 0 | 200 | 36 | 50 | 88 | 15 | 54 | 55 |
| Analysis4 | 48 | 1.3 | 13 | 0.9 | 8 | 0.23 | 7 | 10 | 2.4 | 1.6 | 0.18 | 0.13 | 0 | 0 | 0 | 23 | 56 | 144 | 3 | 200 | 83 |
| Analysis5 | 50 | 1 | 15 | 0.8 | 11 | 0.21 | 10 | 11 | 2.5 | 0.3 | 0.2 | 0.14 | 0 | 0 | 0 | 29 | 41 | 290 | 3 | 87 | 89 |
| Analysis6 | 47 | 0.6 | 17 | 1 | 11 | 0.2 | 9 | 10 | 2.1 | 2 | 0.09 | 0.23 | 0 | 0 | 0 | 60 | 60 | 138 | 7 | 100 | 46 |
| Analysis7 | 50 | 0.5 | 17 | 1 | 9 | 0.14 | 10 | 12 | 3.1 | 1.9 | 0.1 | 0.16 | 0 | 0 | 0 | 39 | 34 | 150 | 18 | 272 | 90 |
| Analysis8 | 47 | 1.4 | 15 | 0.6 | 11 | 0.17 | 12 | 9 | 2 | 1 | 0.14 | 0.21 | 0 | 0 | 0 | 65 | 70 | 147 | 4 | 172 | 57 |
| Analysis9 | 52 | 1.5 | 17 | 0.5 | 9 | 0.21 | 9 | 8 | 2.6 | 0.8 | 0.11 | 0.24 | 0 | 0 | 0 | 95 | 30 | 164 | 12 | 68 | 86 |
| Analysis10 | 48 | 1.2 | 14 | 0.5 | 11 | 0.2 | 10 | 10 | 3.2 | 1.7 | 0.19 | 0.16 | 0 | 0 | 0 | 51 | 47 | 93 | 18 | 42 | 64 |
| Analysis11 | 49 | 0.6 | 14 | 0.9 | 9 | 0.11 | 11 | 9 | 1.6 | 1.6 | 0.07 | 0.13 | 0 | 0 | 0 | 99 | 42 | 104 | 5 | 145 | 95 |
| Analysis12 | 48 | 1.1 | 14 | 0.7 | 11 | 0.17 | 8 | 8 | 2.7 | 1.9 | 0.08 | 0.12 | 0 | 0 | 0 | 58 | 63 | 196 | 18 | 258 | 63 |

**Figure 2.3.** Window for selecting an analysis from the imported datafile.

### *2.1.2.1. Calculating multiple analyses from the loaded data file*

Petrolog4 offers an option of calculating all analyses in the data file using the same set of calculation parameters. The data file can also contain columns that store parameters for stopping calculations for each analysis (see Section 4.1.9 for details).

When a data file is loaded, the ‘Calculate all analyses’ check box becomes active (Fig. 2.2) if there is more than one analysis in the file.

<u>***Note:***</u> When the ‘Calculate all analyses’ box is checked, Petrolog4 ignores the composition in the ‘Starting melt composition’ subsection, and instead reads analyses consequently from the loaded data file.

## *2.2. Saving the results of calculations to a file*

Petrolog4 offers three options for saving calculation results for future use.

**I**. During calculations, Petrolog4 continuously prints the state of the system into the Output Section of the Main form (Fig. 1.1). This output can be highlighted within the Output Section by first clicking inside the section and pressing Ctrl+A, and then copied (Ctrl+C) to the clipboard and pasted into a text editor.

**II**. By default, Petrolog4 always saves the results into a number of comma-separated values files named ‘Ptl_Otpt_*.csv’. The output file name currently in use is displayed above the Output window on the left side of the Main form (Figs. 1.1, 2.2). The number of files created by Petrolog4, and their structure, depend on the chosen calculation option and will be described later in this manual.

<u>***Note:***</u> Output files saved during modelling crystallisation calculations have ‘FRAC’ added to their name (i.e., ‘Ptl_Otpt_FRAC_*.csv’); output files saved during modelling reverse of fractional crystallisation calculations have ‘REV’ added to their name; output files saved during estimation of melt liquidus association calculations have ‘MLA’ added to their name; output files saved during modelling melt inclusions in olivine have either ‘IRL’ or ‘PIC’ or ‘PCR’ added to their name, depending on the chosen type of calculations.

After the calculations are completed, the saved files can either be opened manually (not recommended) or can be imported into Excel (recommended) by using the ‘Export to MS Excel’ section of the Main Menu (Figs. 1.1, 2.2). The latter creates an Excel workbook with several worksheets containing all the details of the calculation. To export the latest results, use ‘Results of the last calculation’ option.

***Note:*** When the default output file name is used, the output files from the last calculation will be overridden when a new calculation of the same type starts. If you would like to keep the results of the previous calculation, export them to Excel prior to starting a new calculation.

**III**. Petrolog4 can save the output into .csv files with a user-specified name.

To specify the output file name, use the ‘File for output…’ option in the ‘File’ section of the Main Menu on the Main form (Fig. 2.2). Type in the desired file name into the ‘File name:’ field on the ‘Save As’ dialog form that opens, choose the folder for saving the file, and press the ‘Save’ button. Do not provide an extension for the file name as it will be ignored.

These files can be opened or loaded in Excel in a similar way as described for option **II**. You can choose either ‘Results of previous calculations’ or ‘Results of the last calculation’. When exporting results of a previous calculation, a dialog window pops-up where the user should select the file to open as explained for each calculation type later in this manual. Results of the last calculation are exported automatically.

***Note:*** If the user-specified file name is not changed before starting a new calculation of the same type, results of the previous calculation will be overwritten at the start of the new calculation.

### *2.3. Reading data files and saving the results of calculations when using non-English language versions of Windows*

Petrolog4 allows the user to choose the decimal separator and the delimiter for the comma-delimited-values text files (*.csv). The default settings are ‘.’ for the decimal separator and ‘,’ for the *.csv delimiter, that are default settings for English language versions of Windows. The user can change the separator to ‘,’ and the delimiter to ‘;’ in the Petrolog Options form (see Section 1.2) that can be displayed by choosing the ‘Options’ item in the ‘Tools’ section of the Main Menu.

***Note:*** These settings only affect the format of files read and written by Petrolog4. They have no effect on the display of numbers within the software.

## 3. Defining and storing sets of values of distribution coefficients (D) for trace and volatile elements

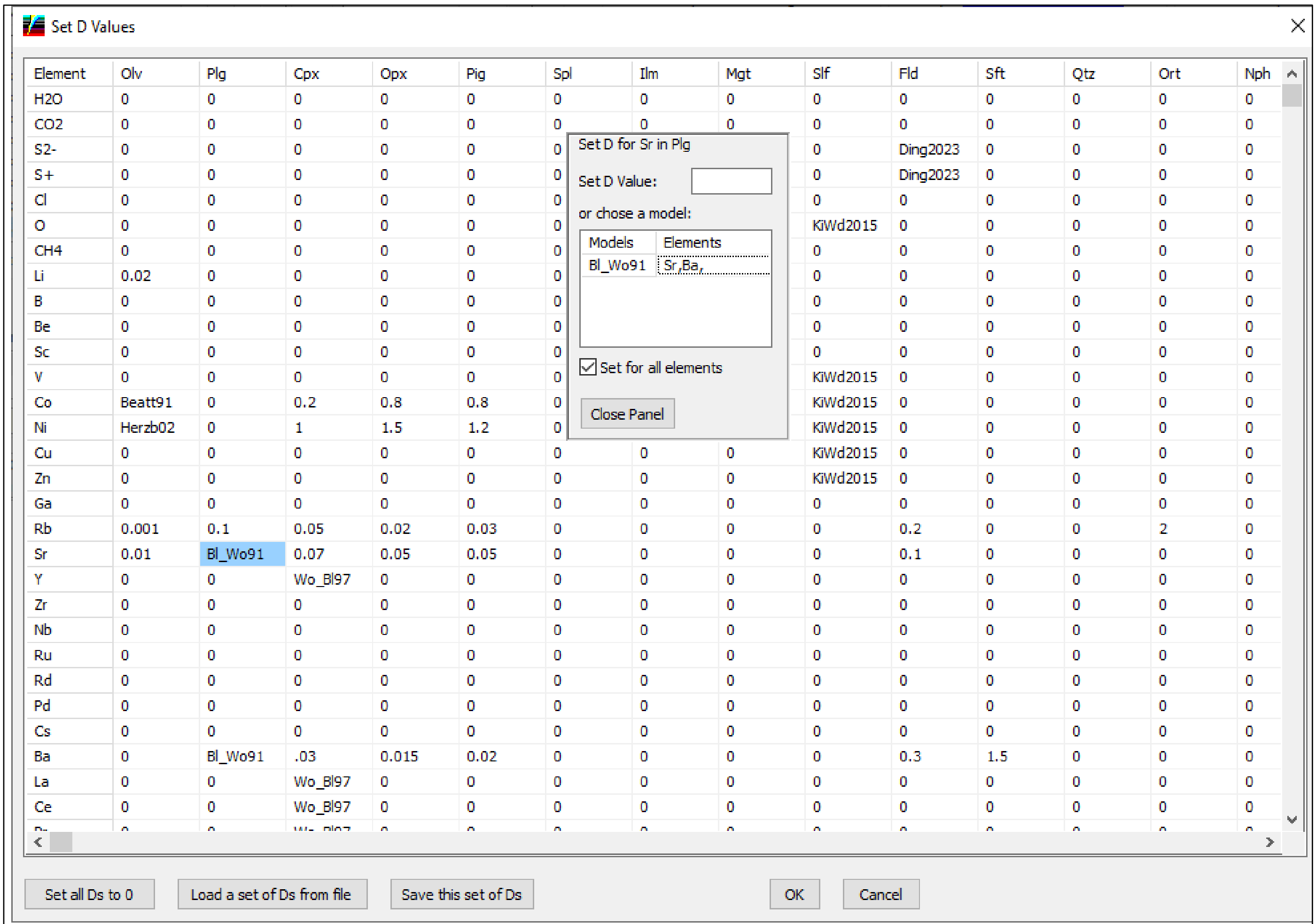
In general, distribution coefficients (D) are defined as $D^{i}_{phase} = C^{i}_{phase} / C^{i}_{melt}$, where '$C^{i}$' are concentrations of element 'i' in a phase (e.g., plagioclase, fluid, sulphide melt, etc.) and in the silicate melt.

Petrolog4 provides three approaches to handling distribution coefficients.

**I**. Some of the phase-melt equilibrium models incorporate some trace and volatile elements. When such models are chosen for calculations, by default the concentrations of these elements in the phase will be calculated following the approach used in the model (e.g., the model of Herzberg and O'Hara, 2002 for olivine melt-equilibrium incorporates Ni; the model of Kiseeva et al., 2015 for sulphide-melt – silicate-melt equilibrium incorporates V, Co, Ni, Cu, Zn, Pb).

**II**. One can set a constant D value, which is then used in the calculation(s).

To enter D values, use the 'Set D values' option in the 'Tools' menu (Fig. 1.2). A pop-up window 'Set D Values' appears (Fig. 3.1).




| Element | Olv | Plg | Cpx | Opx | Pig | Spl | Ilm | Mgt | Slf | Fld | Sft | Qtz | Ort | Nph |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H2O | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| CO2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| S2- | 0 | 0 | 0 | 0 | 0 | 0 | | | 0 | Ding2023 | 0 | 0 | 0 | 0 |
| S+ | 0 | 0 | 0 | 0 | 0 | 0 | | | 0 | Ding2023 | 0 | 0 | 0 | 0 |
| Cl | 0 | 0 | 0 | 0 | 0 | 0 | | | 0 | 0 | 0 | 0 | 0 | 0 |
| O | 0 | 0 | 0 | 0 | 0 | 0 | | | KiWd2015 | 0 | 0 | 0 | 0 | 0 |
| CH4 | 0 | 0 | 0 | 0 | 0 | 0 | | | 0 | 0 | 0 | 0 | 0 | 0 |
| Li | 0.02 | 0 | 0 | 0 | 0 | 0 | | | 0 | 0 | 0 | 0 | 0 | 0 |
| B | 0 | 0 | 0 | 0 | 0 | 0 | | | 0 | 0 | 0 | 0 | 0 | 0 |
| Be | 0 | 0 | 0 | 0 | 0 | 0 | | | 0 | 0 | 0 | 0 | 0 | 0 |
| Sc | 0 | 0 | 0 | 0 | 0 | 0 | | | 0 | 0 | 0 | 0 | 0 | 0 |
| V | 0 | 0 | 0 | 0 | 0 | 0 | | | KiWd2015 | 0 | 0 | 0 | 0 | 0 |
| Co | Beatt91 | 0 | 0.2 | 0.8 | 0.8 | 0 | | | KiWd2015 | 0 | 0 | 0 | 0 | 0 |
| Ni | Herzb02 | 0 | 1 | 1.5 | 1.2 | 0 | | | KiWd2015 | 0 | 0 | 0 | 0 | 0 |
| Cu | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | KiWd2015 | 0 | 0 | 0 | 0 | 0 |
| Zn | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | KiWd2015 | 0 | 0 | 0 | 0 | 0 |
| Ga | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Rb | 0.001 | 0.1 | 0.05 | 0.02 | 0.03 | 0 | 0 | 0 | 0 | 0.2 | 0 | 0 | 2 | 0 |
| Sr | 0.01 | Bl_Wo91 | 0.07 | 0.05 | 0.05 | 0 | 0 | 0 | 0 | 0.1 | 0 | 0 | 0 | 0 |
| Y | 0 | 0 | Wo_Bl97 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Zr | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Nb | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ru | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Rd | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Pd | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Cs | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ba | 0 | Bl_Wo91 | .03 | 0.015 | 0.02 | 0 | 0 | 0 | 0 | 0.3 | 1.5 | 0 | 0 | 0 |
| La | 0 | 0 | Wo_Bl97 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ce | 0 | 0 | Wo_Bl97 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

**Figure 3.1.** Form for defining D values to be used in calculations. If a model for D values for an element in a phase is available, a popup window will appear in the middle of the form when the use clicks on the cell corresponding for such an element, as shown for Sr in plagioclase. See text for details.
***Note:*** Although this form lists methane ($CH_4$), the current version of Petrolog4 does not incorporate methane and this row is disabled on the form.

Constant D values for any phase/element can be set by entering them into the corresponding cells (Fig. 3.1). The entered D values must be calculated using <u>*weight units*</u> of concentration.

If any of the currently chosen models of phase-melt equilibrium incorporate trace elements in addition to major elements, these models will be displayed in the corresponding cells on the form. For the example shown on Figure 3.1, Kiseeva et al. (2015) model is chosen for sulphide-melt – silicate-melt equilibrium, and

Herzberg and O'Hara (2002) model is chosen for olivine-melt equilibrium. As a result, 'Herzb02' is displayed in the Ni cell for olivine and 'KiWd2015' is displayed for the V, Co, Ni, Cu, Zn cells for sulphide.

***Note:*** Oxygen is considered a major element in all phases but sulphide, and thus a D value for oxygen can only be set for sulphide.

***Note:*** Reduced sulphur is considered a major element in sulphide, and thus a D value for reduced sulphur can be set for all phases but sulphide.

***Note:*** Although it is possible to set D values for $H_2O$ and $CO_2$ in the fluid phase, if the chosen model for the fluid phase incorporates either of these elements they would be considered as major elements for the fluid phase, and thus the entered D values will be ignored and the concentrations calculated be the chosen model will be used.

***Note:*** Oxidised sulphur is considered a major element in sulphate, and thus a D value for oxidised sulphur can be set for all phases but sulphate.

***Note:*** If desired, the displayed model names can be overwritten by a constant D value by entering the value into the corresponding cell.

**III**. Petrolog4 allows for using models that define D values for an element in a phase as a function of various parameters, such as melt composition, temperature, phase composition, etc. D models available in the current version of Petrolog4 are listed in Appendix 1.

If D models are available for an element in a phase, a pop-up window will appear when clicking on the cell for that element/phase (Fig. 3.1). The pop-up window will display all available models for the element in the phase. All elements available in the model are listed (e.g., Ba and Sr are available in the Blundy and Wood, 1991 model for plagioclase, Fig. 3.1). Clicking on *the list of elements* (not the name of the model) will apply the model to the selected element. If the 'Set for all elements' checkbox is ticked *before selecting a model,* the model will be applied for all elements that are part of this model, not just the one that was clicked on the form. If required, D values for individual elements in the list can be later set to constant values by entering the D value into the 'Set D Value:' box and pressing the 'Close panel' button. This will not affect the application of the chosen model to the remaining elements in the list.

***Note:*** The pop-up window only appears when clicking on an element for which a D model is available. The pop-up window disappears after clicking on a cell for an element for which no D models are available in Petrolog4.

***Note:*** Petrolog4 assigns a charge of +4 to the oxidised sulphur in the fluid. In all other phases, the charge of oxidised sulphur is +6. Thus, the D value for oxidised sulphur between the fluid and silicate melt is defined as $C^{SO_2}{}_{fluid}$ / $C^{SO_3}{}_{melt}$ .

To save the chosen set of D values and models, press the 'Save this set of Ds' button. In the dialog form that appears, enter a file name and press Save.

***Note:*** Petrolog4 assigns .PtlDSet extension to files with D values.

To load a saved set of D values, press the 'Load a set of Ds from file' button, chose the file in the dialog window, and press Open.

To finish editing D values, close the form by pressing the 'Ok' button. To close the form without applying any of the changes, press the 'Cancel' button.

# 4. Modelling crystallisation

To model crystallisation, chose 'Crystallisation' tab of the Main form (Figs. 1.1, 1.2, 2.2).

## *4.1. Setting calculation parameters*

The following calculation parameters can be set before starting calculations:

- set of phases involved in calculations;
- phase-melt equilibrium model for each phase;
- extent of fractionation for each phase;
- melt oxidation state;
- fluid and sulphur saturation models;
- pressure;
- melt density and viscosity models;
- calculation step;
- conditions for stopping calculations;
- conditions for the output of results during calculation
- conditions for modelling replenishment.

These are described in detail below.

***Note:*** Petrolog4.zip file contains recommended predefined sets of parameters for modelling crystallisation of several major geodynamic types of magmas such as mid-ocean ridge basalts and subduction-related magmas. These sets of parameters can also be downloaded from the Petrolog4 website.

### 4.1.1. Choosing phases and phase-melt equilibrium models

Phases and models are chosen in the 'Models for phase-melt equilibrium' subsection of the Parameters Section (Figs. 1.1, 1.2).

When 'Press to Select' is written in the 'Model' field next to a phase name when 'Start calculations' button is pressed, this phase *will not* be included in calculations. If a model abbreviation is written next to a phase name (e.g., Ford et al., 1983 next to Olivine on Fig. 1.1), the phase *will* be included in calculations.

***Note:*** Selecting a phase for calculations *does not guarantee* that it will appear on the liquidus during calculations. Petrolog4 algorithm determines the order of crystallisation based on the chosen parameters.

To choose a model for a phase, click on the 'Model' field for that phase (Figs. 1.1, 1.2). A pop-up window with a list of available models for this phase will appear (Fig. 4.1).

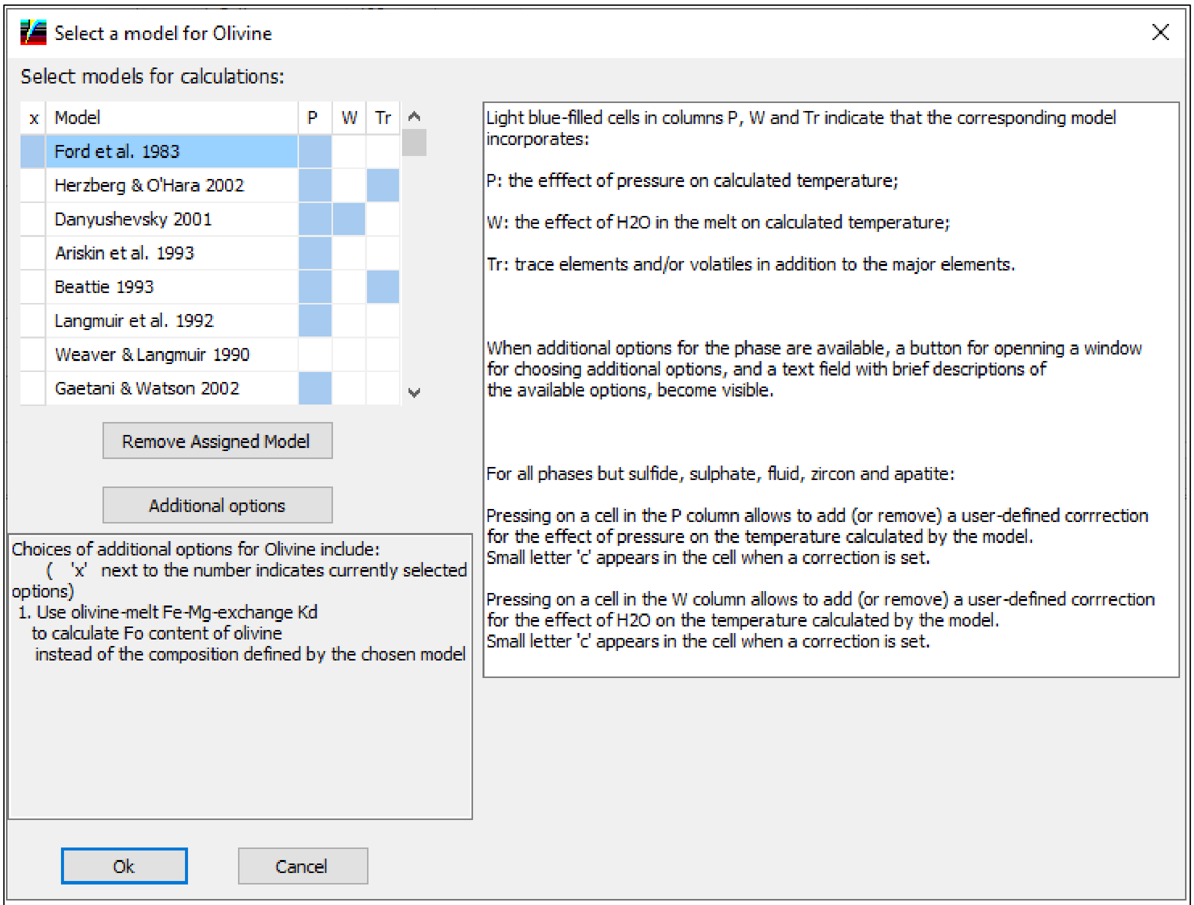



**Figure 4.1.** Window for choosing an olivine-melt model to be used in calculations.

This window contains a table with 4 columns. Text box on the right provides a brief explanation on how to use the form and interpret the information shown on the form.

Column ‘Model’ lists model abbreviations. Column ‘P’ indicates whether a model incorporates the effect of pressure on the phase-melt equilibrium (the cell is coloured light blue), or alternatively it is designed for the atmospheric pressure only (the cell has white background). Column ‘W’ indicates whether a model incorporates the effect of $H_2O$ on phase -melt equilibrium (the cell is coloured light blue), or alternatively it is designed for anhydrous conditions only (the cell has white background). Column ‘Tr’ indicates whether a model incorporates any trace or volatile elements. If the ‘Tr’ cell for a model is coloured light blue, the model incorporates some of those elements. Blue rectangle to the left of the Ford et al. (1983) cell indicates that this model is currently chosen for calculations.

When additional options for the current phase are available (See Section 4.1.1.1), the ‘Additional options’ button and a text field with brief descriptions of the available options are displayed on the form.

Clicking on the name of a different model will change selection to that model.

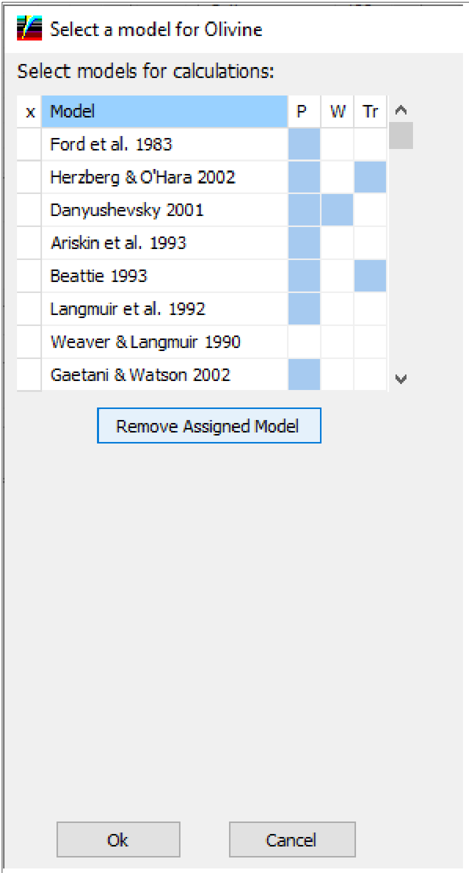



**Figure 4.2.** Window for choosing an olivine-melt model with no model selected.

Clicking on the ‘Remove Assigned Model’ button will deselect the selected model and not select any other model (Fig. 4.2). When no model is assigned, the ‘Additional Options’ button is not shown even when such options are available for the phase. Clicking on the ‘Ok’ button when no model is selected will result in ‘Press to Select’ showing next to the phase in the ‘Models for phase-melt equilibrium’ subsection of the Main form (Figs. 1.1, 1.2, 2.2).

Clicking on the ‘Cancel’ button will close the form without applying any of the changes made.

To set a model for another phase, click on the ‘Model’ field for that phase in the ‘Models for phase-melt equilibrium’ subsection of the Parameters Section (Figs. 1.1, 1.2, 2.2).

***Note:*** The available models for sulphide, sulphate, zircon and fluid calculate the compositions of these phases for the given pressure, temperature and melt composition. Thus, including these models in calculations requires choosing at least one silicate or oxide mineral-melt model to enable temperature calculations.

***Note:*** Before starting calculations: 1) when either $H_2O$ or $CO_2$ are present in the starting composition, the user must choose a model for fluid-melt equilibrium; 2) when S is present in the starting composition, the user must choose a sulphide melt – silicate melt and a sulphate melt – silicate melt equilibrium model; 3) when Zr is present in the starting composition, the user must choose a zircon melt – silicate melt equilibrium model.

#### *4.1.1.1. Additional options for calculating phase compositions*

In the current version, additional options are available for olivine and plagioclase. When options are available, the ‘Additional options’ button and a text field with brief descriptions of the available options are displayed on the form (Fig. 4.1). When an additional option is chosen, ‘x’ appears next to its description in the text field. Clicking on the ‘Additional options’ button opens the Additional Options form (Fig. 4.3).

When choosing a model for olivine-melt equilibrium, the ‘Use olivine-melt Fe-Mg-exchange Kd to calculate olivine Fo content’ check box on the Additional Options form can be used to set an olivine-melt Fe-Mg exchange Kd value for calculation of olivine composition. This calculated composition will be used instead of the composition calculated by the selected olivine-melt model.

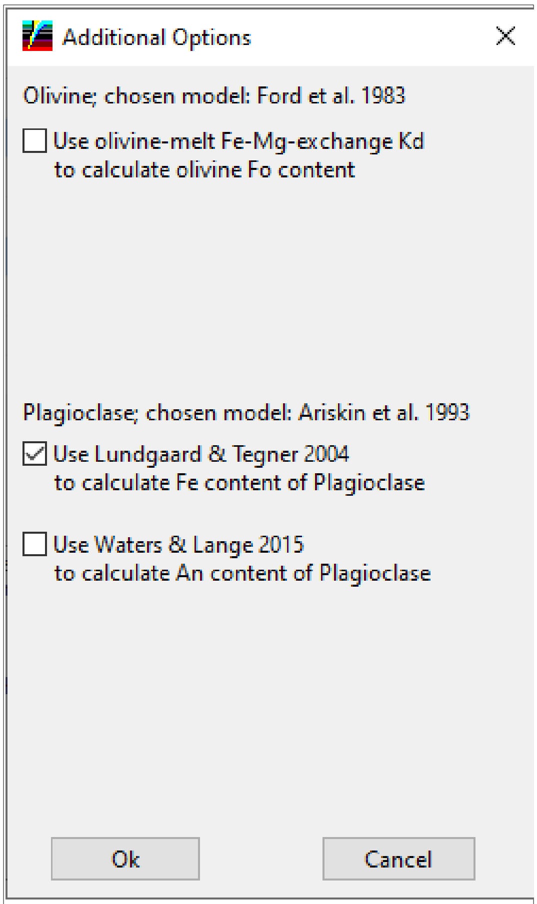



**Figure 4.3.** Additional Options window.

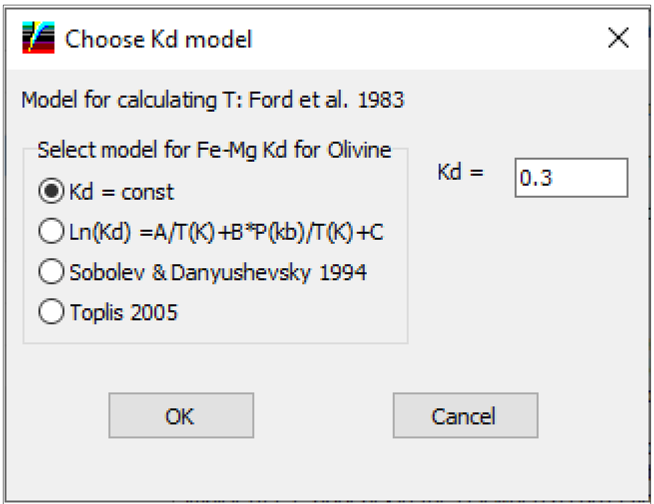



**Figure 4.4.** Window for choosing a value for the olivine-melt Fe-Mg exchange coefficient (Kd).

***Note:*** When calculating olivine compositions using a Kd value, the olivine-melt equilibrium model chosen in the 'Select a model for Olivine' window (Fig. 4.1) is used for calculating olivine crystallisation temperature.

When the box is switched to 'checked', a pop-up window appears that is used to determine how the Kd values are determined (Fig. 4.4). Four options are available for calculating Kd values:

(1) 'Kd = const': When this option is chosen, a Kd value must be entered in the box to the right, that will be used in calculations.

(2) 'Ln(Kd) = A/T(K)+B*P(kbar)/T(K)+C': When this option is chosen, values for coefficients A, B and C must be provided. The default values correspond to a Kd value of 0.3.

(3) 'Sobolev & Danyushevsky 1994': When this option is chosen, Kd values will be calculated following the method described in the Appendix 1 of Sobolev and Danyushevsky (1994).

(4) 'Toplis 2005': When this option is chosen, Kd values will be calculated using the method of Toplis (2005).

Pressing the 'Cancel' button will close the form without applying any of the changes made.

To deselect the Kd option, uncheck the 'Use olivine-melt Fe-Mg-exchange Kd to calculate olivine Fo content' box by clicking on it when it is checked.

#### *4.1.1.2. Additional options for plagioclase*

When selecting a plagioclase-melt equilibrium model, the user is given a choice of using the Waters and Lange (2015) model to calculate plagioclase anorthite content, and Lundgaard and Tegner (2004) model for ferric and ferrous iron equilibrium between plagioclase and melt (Fig. 4.3).

When the Waters and Lange (2015) model an option is selected (the checkbox on the form is checked), the anorthite content in plagioclase will be calculated by using this model, overriding the plagioclase composition calculated by the chosen plagioclase-melt equilibrium model. The chosen plagioclase-melt equilibrium model will be used for calculating plagioclase crystallisation temperature, but not the composition.

***Note:*** The Waters and Lange (2015) model is not applicable to all melt compositions and may fail to calculate anorthite content of plagioclase. In such cases, calculation of plagioclase compositions will revert to the chosen plagioclase-melt equilibrium model, and the option to use the Waters and Lange (2015) model will be deselected.

When the Lundgaard and Tegner (2004) model is selected (the checkbox on the form is checked), the Fe content in plagioclase will be calculated by using this model, overriding the Fe content calculated by the chosen plagioclase-melt equilibrium model (if the chosen model incorporates Fe content in plagioclase. This option is provided as most available plagioclase-melt models do not calculate Fe content in plagioclase.

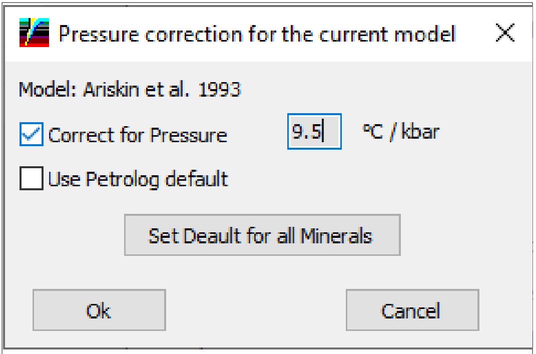



**Figure 4.5.** Window for setting a correction for the effect of pressure on the calculated liquidus temperature.

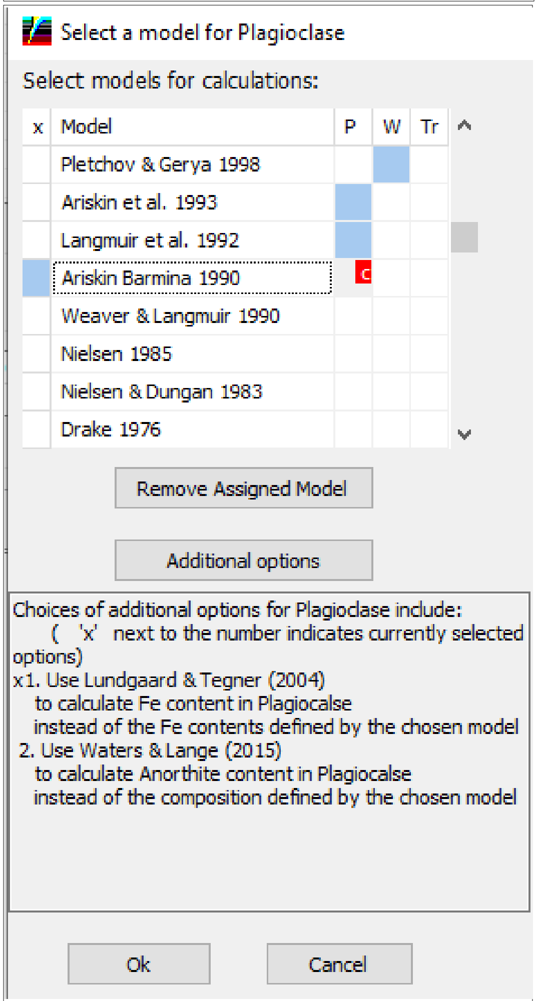



**Figure 4.6.** Window for choosing a model for plagioclase-melt equilibrium; 'c' in column 'P' indicating that a pressure correction is set.

#### *4.1.1.3. Setting a pressure correction to the temperature calculated by the chosen model*

Petrolog4 offers an option to introduce a linear correction for the effect of pressure on the pseudo-liquidus temperature calculated by a model. A separate correction value can be set for each mineral involved in calculations. To set a correction, click on the 'P' cell next to the chosen model (Fig. 4.1). This opens a pop-up window where a correction value in degrees/kbar can be set (Fig. 4.5).

The user can set a value for the correction, or chose to use the Petrolog4 default correction value, by clicking on 'Use Petrolog Default' (See Appendix 1 for Petrolog Default corrections).

Pressing the 'Cancel' button will close the form without applying any changes.

When correction is set, a small letter 'c' on red background appears in the 'P' cell next to the chosen model (Fig. 4.6).

***Note:*** Since sulphide melt, sulphate, fluid, zircon and apatite models do not calculate crystallisation temperatures, a pressure correction cannot be set for these phases.

***Note:*** If the 'Ok' button is clicked when the correction value is 0, no correction is applied, even if the 'Correct for Pressure' checkbox is checked.

***Note:*** If a chosen model incorporates the effect of pressure (e.g., models of Langmuir et al. 1992 and Ariskin at al. 1993 on Fig. 4.6), then the option 'Apply H2O and P Corrections to All Models' (Fig.1.3) defines whether the correction will apply. When the option is selected, the correction will apply to models that incorporate pressure.

***Note:*** Once chosen, a correction applies to all models, i.e., if the phase-melt model is changed after the correction is set, the correction will be transferred to the new model. To remove the correction, open the 'Pressure correction' window again (Fig. 4.5) and uncheck the 'Correct for Pressure' box. The small letter 'c' in the 'P' cell will disappear returning the form to its original state.

***Note:*** Setting a user-defined correction for the effect of pressure on the pseudo-liquidus temperature, does not affect the mineral composition that the chosen model calculates.

#### *4.1.1.4. Setting an $H_2O$ correction to the temperature calculated by the chosen model*

As only a few models available in Petrolog4 incorporate the effect of melt $H_2O$ content on pseudo-liquidus temperature and/or composition of crystallizing phases (e.g., Plechov and Gerya, 1998; Danyushevsky, 2001; Putirka, 2005), Petrolog4 allows the user to introduce corrections to the 'anhydrous' models for the effect

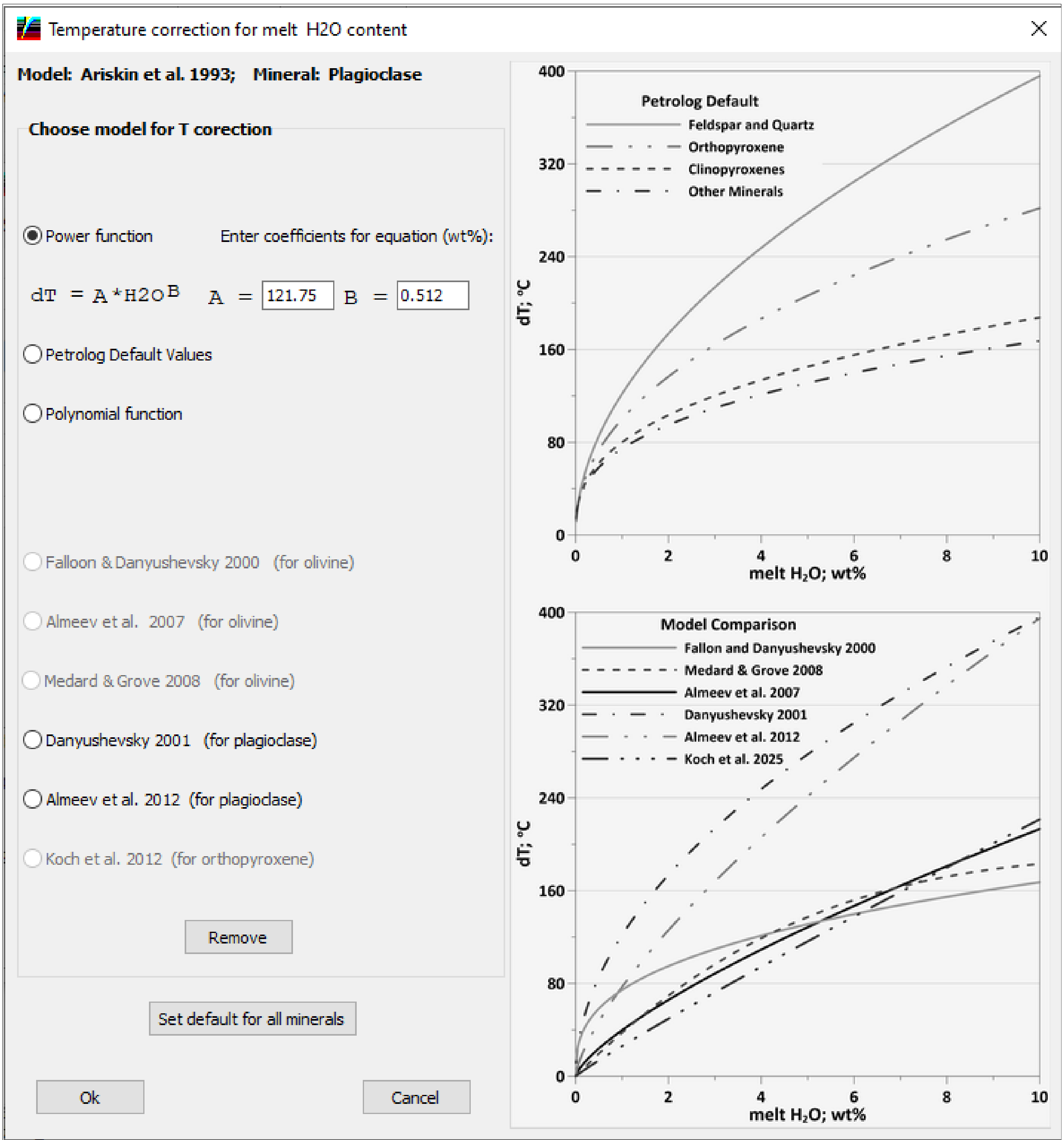



**Figure 4.7.** Window for setting a correction for the effect of $H_2O$ on liquidus temperature of plagioclase.

of $H_2O$ on calculated temperatures, to enable calculations under hydrous conditions using models developed for anhydrous conditions.

To set a correction, click on the 'W' cell next to the chosen model (Figs. 4.1, 4.6). This opens a pop-up window 'Temperature correction for melt H2O content' (Fig. 4.7) which is used to set the correction.

***Note:*** Similarly to the pressure correction described above, applying an $H_2O$ correction to the calculated temperature does not affect the calculated phase compositions. Also similarly to the pressure correction, an $H_2O$ correction cannot be set for sulphide melt and fluid models.

***Note:*** Similarly to the pressure correction described above, if a chosen model incorporates the effect of $H_2O$, then the option 'Apply H2O and P Corrections to All Models' (Fig. 2.4) defines whether the correction will apply. When selected, the correction will apply to models that incorporate the effect of $H_2O$.

Petrolog4 offers several options for setting an $H_2O$ correction: user defined power or polynomial functions, Petrolog4 default corrections, and published models for setting $H_2O$ correction that are currently available for olivine, plagioclase and orthopyroxene. Petrolog4 default corrections are plotted on the top graph on the form. A comparison between published models is plotted on the bottom plot on the form. The list of available models for $H_2O$ corrections and parameters for Petrolog4 default corrections are presented in Appendix 1.

A polynomial correction can be set in a form: dT (°C) = A * ($H_2O$ wt.%)$^3$ + B * ($H_2O$ wt.%)$^2$ + C * ($H_2O$ wt.%).

***Note:*** if desired, a linear correction can be set by using either power or polynomial corrections and setting B to 1 for the former or setting A and B to 0 for the latter.

When a correction is set, small letter 'c' on red background appears in the 'W' cell next to the chosen model (Fig. 4.8).

***Note:*** Once chosen, a correction, applies to all models, i.e., if the phase-melt model is changed after the correction is set, the correction will be transferred to the new model. To remove the correction, open the 'Temperature correction for melt H2O content' window again (Fig. 4.7) and press 'Remove' button. The small letter 'c' in the 'W' cell will disappear returning the form to its original state.

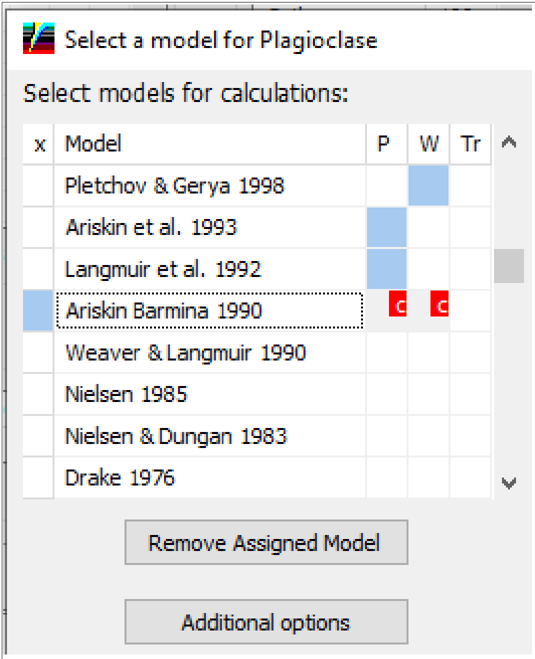



**Figure 4.8.** Window for choosing a model for plagioclase-melt equilibrium with 'c' in columns 'P' and 'W' next to the chosen model indicating that a pressure correction and an $H_2O$ correction were set.

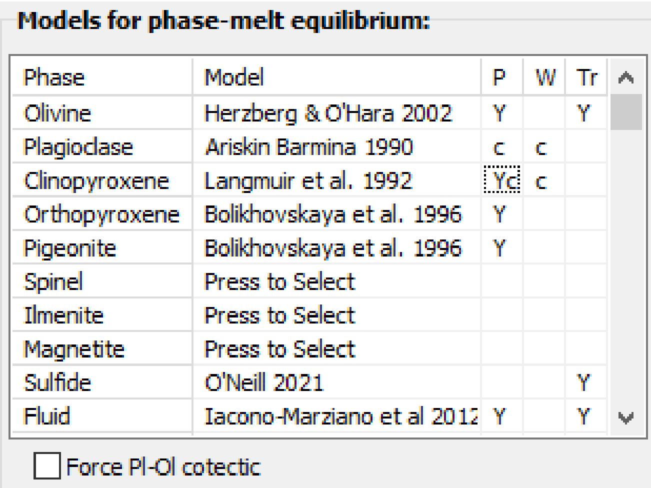



**Figure 4.9.** The 'Models for phase-melt equilibrium' subsection of the Parameters Section showing selected mineral-melt models; whether the selected models incorporate pressure, $H_2O$ and trace elements ('Y'); and which models have corrections set for the effects of pressure and $H_2O$ ('c').

The 'Mineral-melt models' subsection of the Parameters Section (Fig. 1.1) displays the models chosen for each mineral and uses columns 'P', 'W', and 'Tr' to indicate whether the chosen models incorporate effects of pressure and/or $H_2O$, and/or trace elements, and whether any user-defined correction are set for the effects of pressure and melt $H_2O$ contents. Capital 'Y' is used to indicate that a model includes a corresponding effect, whereas 'c' is used to indicate that a correction is set (Fig. 4.9).

#### *4.1.1.5. Calculating an olivine - plagioclase ± clinopyroxene cotectic crystallisation.*

Petrolog4 offers an option of forcing the starting composition on an olivine-plagioclase (+/- clinopyroxene) cotectic by adjusting melt $H_2O$ content, following the method of Danyushevsky (2001). The essence of the approach is to first calculate the amount of $H_2O$ which is required for the starting composition to lie on an olivine-plagioclase cotectic, and then to model crystallisation with this $H_2O$ content in the starting composition, so that the composition is cotectic from the onset of crystallisation. (see Danyushevsky, 2001 for a detailed description of the approach). The set of minerals is limited to olivine, plagioclase and clinopyroxene, and the set of models is limited to those from Danyushevsky (2001).

To use this option, check the ‘Force Pl-Ol cotectic’ checkbox in the ‘Models for phase-melt equilibrium’ subsection of the Parameters Section (Fig. 4.9).

***Note:*** This option should be used for MORB and BABB compositions only, as the models of Danyushevsky (2001) have not been calibrated outside that compositional range.

***Note:*** When using this option, calculation pressure should be set at a value that ensures that the melt $H_2O$ content required is less than the saturation value (see section 4.1.4).

### 4.1.2. Setting extent of fractionation for each phase

Petrolog4 allows for a specific extent of fractionation to be set for each using using the ‘Extent of fractionation (%)’ subsection of the Parameters Section (Figs. 1.1, 1.2, 2.2). By default, a value of 100% is assigned to each phase, corresponding to the case of pure fractional crystallisation. When modelling pure fractional crystallisation, a phase is ‘removed’ from contact with melt and placed into the ‘cumulate’ part of the system, thus retaining its original composition.

If 0% is assigned to a phase, this corresponds to pure equilibrium crystallisation. When modelling equilibrium crystallisation, the total amount of the crystallised phase remains in equilibrium with the residual melt, thus continuously changing its composition. No ‘cumulate’ is formed during equilibrium crystallisation.

When a number between 0 and 100 is entered for a phase, this proportion of the phase is continuously ‘removed’ from contact with the melt preserving its composition, whereas the remainder of the phase re-equilibrates with the continuously evolving melt. See Danyushevsky and Plechov (2011) for further details of the approach.

### 4.1.3. Setting pressure

Pressure to be used during calculations is set in the ‘Pressure’ subsection of the Parameters Section (Figs. 1.1, 1.2, 2.2). A value at the onset of calculations (in kbar) can be set in the ‘Initial P (kbar)’ textbox within this subsection.

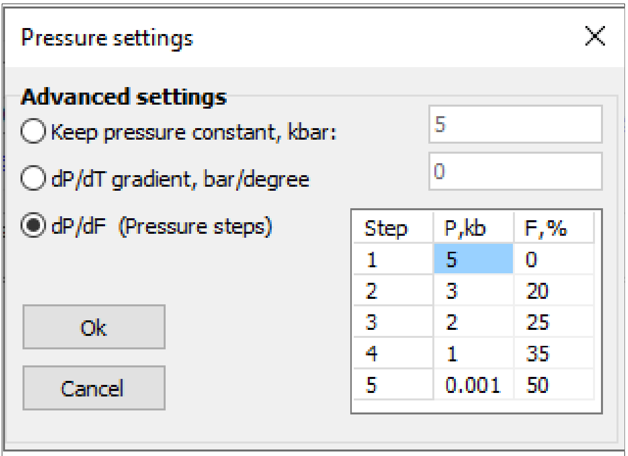



**Figure 4.10.** The ‘Pressure settings’ window showing three available options for controlling pressure during calculations.

***Note:*** The data file can contain a column that defines pressure values to be used in calculations that can differ for each analysis. The values should be in kbar (1 kbar = 0.1 GPa). This column should have the following name in the header row: P KBAR or P_KBAR or PRESSURE.

To define changes to crystallisation pressure during calculations, click on the blue text label below the ’Set Pressure behaviour:’ text label in this subsection. This will open the ‘Pressure settings’ pop-up window (Fig. 4.10).

By default, the ‘Keep pressure constant’ option is chosen.

The ‘dP/dT gradient, bar/degree’ option allows for pressure to be continuously changed at a fixed rate as a function of temperature. A positive value corresponds to decreasing pressure during crystallisation. If pressure reaches 1 bar before the end of the calculations, it will remain at 1 bar for the remainder of the calculations. Setting a negative value for the gradient would result in pressure increasing during crystallisation calculations.

The ‘Pressure steps’ option allows for changing pressure during calculations as a function of the degree of fractionation. Up to four intervals with specific dP/dF values can be set. The dP/dF value for an interval is calculated from the P and F values set as the boundary conditions for this interval. The dP/dF value can equal 0 (pressure is constant) for any number of intervals. To set it to 0, the ‘P,kb’ value should be the same at the start and end of the fractionation interval. If the F value at the end of the last step is lower than the final F value during calculations, the pressure value at the last step will be used until the end of fractionation calculations.

The displayed text in the blue text label in the subsection reflects the chosen pressure option: 'Keep constant', 'dP/dT = 'Value', or 'dP/dF.

#### 4.1.4. Setting fluid, sulphur zircon and apatite saturation models

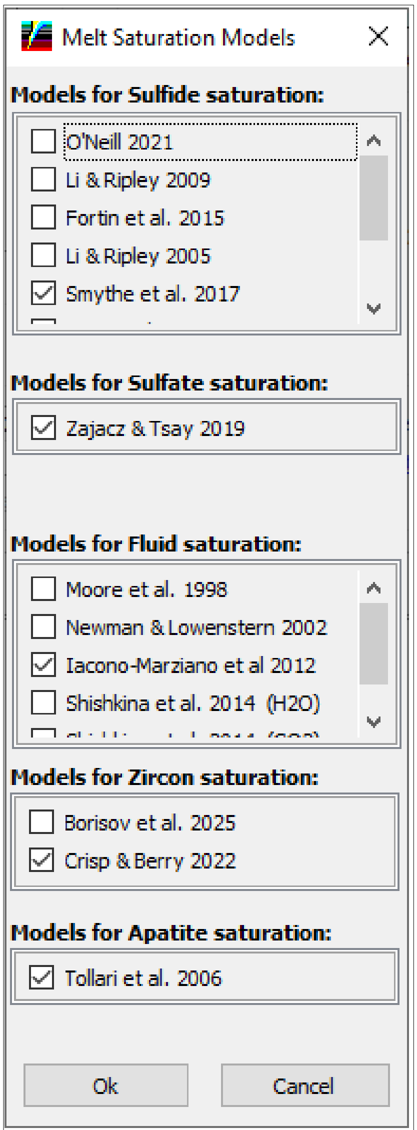



**Figure 4.11.** Window for choosing melt Saturation models.

Performing calculations in Petrolog4 requires that saturation models for fluid sulphur and zircon in the melt are selected. When software starts, default models are automatically selected. The selected models are displayed in the 'Saturation Models' subsection of the Parameters section of the Main form (Figs 1.1, 1.2, 2.2). The selected models can be changed by clicking the blue 'Change Saturation Models:' text label in this subsection to open the 'Melt Saturation Models' pop-up window (Fig. 4.11). The available models are listed in Appendix 1.

Click 'Ok' to save the chosen model. Pressing 'Cancel' closes the form without applying any changes.

When the concentrations of volatile elements ($H_2O$ and $CO_2$), reduced sulphur ($S^{2-}$), oxidised sulphur ($S^{6+}$) or zirconium (Zr) in the melt exceed their solubility values for a given pressure, melt composition and temperature, this leads to appearance of a separate fluid, immiscible sulphide melt, sulphate, or zircon phase, respectively. Similarly to silicate minerals, the fluid, sulphide, sulphate and zircon phases may either remain in the magma or fractionate (see section 4.1.2).

Petrolog4 also offers an option to perform calculation under fluid-saturated and sulphide-saturated conditions. To use these options, check the 'Fluid saturated' and 'Sulphide saturated' checkboxes within the 'Starting melt composition' subsection of the Parameters section of the Main form (Figs. 1.1, 1.2, 2.2).

***Note:*** When $H_2O$ and/or $CO_2$ are present in the starting composition, the user must select a fluid-melt equilibrium model to enable calculations, even if it is not expected that fluid saturation will be reached. When the starting melt composition is significantly fluid oversaturated at the pressure chosen for calculation (i.e., the concentrations of volatiles in the starting composition reflect a pressure value that is 2x higher than the calculation pressure), melt volatile contents ($H_2O$ and $CO_2$) will be adjusted to reflect fluid saturation at the chosen pressure.

***Note:*** When the 'VolatileCalc' model for the fluid composition is chosen, the fluid saturation model of Newman and Lowenstern (2002) will be automatically selected (and vice versa). If calculation pressure is set to < 100 bars, it will be changed to 100 bars as this is the minimum calculation pressure required by the model. If the melt CO2 content decreases below 10 wt. ppm, calculations will be stopped as this model was not meant to be used with such compositions.

***Note:*** When the 'Iacono-Marziano et al 2012' model for fluid composition is selected, the fluid saturation model of Iacono-Marziano et al. (2012) will be automatically selected (and vice versa).

***Note:*** When the 'Pure H2O' model for fluid composition is selected, the fluid saturation model of Moore et al. (1998) will be automatically selected. When either Moore et al. (1998) or Shishkina et al. (2014) (H2O) models are selected, the 'Pure H2O' model for fluid composition will be automatically selected.

***Note:*** When the 'Pure CO2' model for fluid composition is selected, the fluid saturation model of Shishkina et al. (2014) (CO2) will be automatically selected. When Shishkina et al. (2014) CO2 model is selected, the 'Pure CO2' model for fluid composition will be automatically selected.

***Note:*** When S is present in the starting composition, the user must select a sulphide-melt and a sulphate-melt equilibrium models to enable calculations, even if it is not expected that sulphide or sulphate saturation will be reached. When the starting composition is S-oversaturated, the S content will be adjusted to match saturation.

***Note:*** When Zr is present in the starting composition, the user must select a zircon-melt equilibrium model to enable calculations, even if it is not expected that zircon saturation will be reached. When the starting composition is Zr-oversaturated, the Zr content will be adjusted to match saturation.

### 4.1.5. Setting melt oxidation state

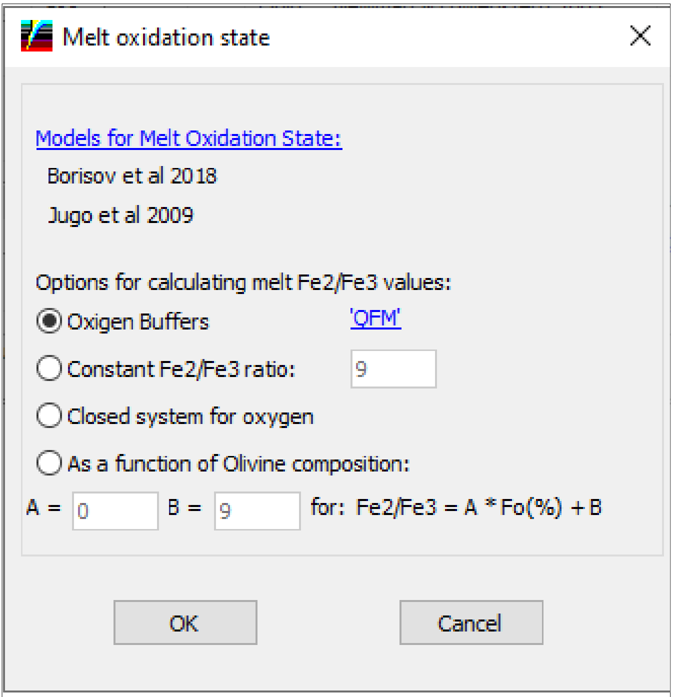



**Figure 4.12.** Window for choosing options for setting melt oxidation state.

The melt oxidation state (i.e., the proportions of $Fe^{2+}$ / $Fe^{3+}$ and $S^{2-}$ / $S^{6+}$ in the melt) during calculations is set in the 'Oxidation state' subsection of the Parameters Section (Figs. 1.1, 1.2, 2.2).

The currently chosen method for controlling melt oxidation state is displayed in the blue text label below 'Calculations performed using:' text label. When Petrolog4 starts, the quartz-magnetite-fayalite (QFM) oxygen buffer is selected by default. To change the selected method, click on the blue text label with the currently selected method, to open the 'Melt oxidation state' pop-up window (Fig. 4.12).

Four options for controlling melt oxidation state are available: **I**) calculation along an oxygen buffer; **II**) calculation with a constant $Fe^{2+}/Fe^{3+}$ value; **III**) calculation assuming a closed system for oxygen, and **IV**) defining melt oxidation state as a function of liquidus olivine composition (Fig. 4.12).

Performing calculations in Petrolog4 requires that models for Fe and S oxidation states in the silicate melt are defined. When software starts, default models are automatically selected. The selected models are displayed in the bottom part of the 'Oxidation state' subsection of the Parameters section of the Main form (Figs 1.1, 1.2, 2.2). The selected models can be changed by clicking the blue 'Change Oxidation Models:' text label in this subsection to open the 'Melt Oxidation State Models' pop-up window (Fig. 4.13). The available models are listed in Appendix 1. This form can also be opened from the 'Melt Oxidation State' window (Fig. 4.12).

**I.** When calculations are performed assuming a closed system for oxygen, the melt oxidation state is controlled by 1) removal of ferrous and ferric Fe by crystallising silicate and oxide minerals; 2) removal of ferrous Fe and $S^{2-}$ by separation of an immiscible sulphide in sulphide-saturated magmas; and 3) by degassing of sulphur species in fluid-saturated magmas. Petrolog4 maintains equilibrium between oxidation states of Fe and S. Petrolog4 does not consider the presence of $Fe^0$ when calculations are performed at strongly reduced conditions.

***Note:*** Sulphur oxidation state in the starting composition is calculated from the melt oxidation state as defined either by the oxygen fugacity or the oxidation state of Fe, regardless of S speciation defined in the starting composition (i.e., regardless of whether sulphur content is entered as S or $SO_3$).

***Note:*** Choosing the 'Closed system for oxygen' option requires that ferric and ferrous Fe contents are defined in the starting composition. If the ferrous Fe content in the starting composition is 0, the calculations will be performed following the Magnetite-Hematite buffer of oxygen fugacity. If the ferric Fe content is set to 0, the calculations will be performed assuming that all Fe and all S in the starting composition are in the reduced form and no oxidised species will be present during fractionation. This latter is identical to choosing Fe3=0 'buffer' option (Fig. 4.14).

**II.** When calculations are performed along an oxygen buffer, to change the selected buffer click on the blue text label next to the 'Oxygen Buffers' bullet point that shows the currently selected buffer (Fig. 4.12). This opens the 'Oxygen Buffers' pop-up window (Fig. 4.14). This window contains a plot comparing oxygen fugacity values along various buffers. Buffer equations are listed in Appendix 1.

To choose a buffer click on one of the check boxes next to the buffer name. You can also specify a shift from the buffer in log10 units of $fO_2$ by specifying a positive or negative value in the 'Buffer shift (log units):' text box. The equations for each of the buffers is listed in Appendix 1.

Close this window by pressing the 'Ok' button. Pressing the 'Cancel' button closes the window without applying the changes made.

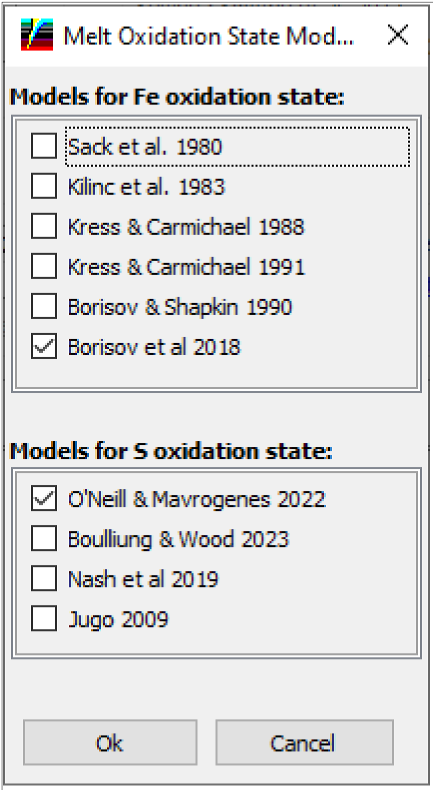



**Figure 4.13.** Window for choosing models setting melt Fe and S oxidation states.

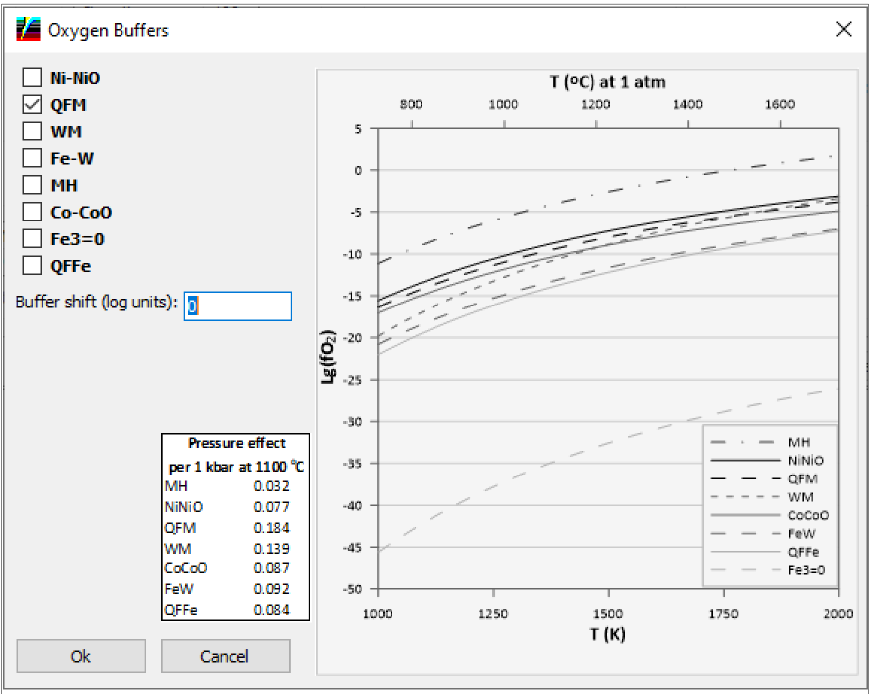



**Figure 4.14.** Window for choosing buffers of oxygen fugacity for controlling melt oxidation state during calculations.

When using an oxygen buffer to define melt oxidation state, the $Fe^{2+}$ / $Fe^{3+}$ and $S^{2-}$ / $S^{6+}$ values in the melt will be calculated from the oxygen fugacity value corresponding to the chosen buffer, following the chosen models for the oxidation state.

**III.** When using a constant $Fe^{2+}$ / $Fe^{3+}$ value to set melt oxidation state, oxygen fugacity and $S^{2-}$ / $S^{6+}$ are calculated from the $Fe^{2+}$ / $Fe^{3+}$ value of the melt following the chosen models for Fe and S oxidation states (Fig. 4.13).

**IV.** If the melt oxidation state is defined as a function of liquidus olivine composition (Fig. 4.12), specify values for coefficients A and B for the equation $(Fe^{2+}/Fe^{3+})_{melt} = A*Fo + B$, where Fo is the proportion of forsterite in the liquidus olivine in mol%. For a detailed description of this technique, see Danyushevsky and Sobolev, 1996. When using this option to set melt oxidation state, oxygen fugacity and $S^{2-}$ / $S^{6+}$ are calculated from the $Fe^{2+}$ / $Fe^{3+}$ value of the melt following the chosen model for Fe oxidation state (Fig. 4.13).

***Note:*** This option is only available when olivine has been chosen for calculations in the 'Models for phase-melt equilibrium' subsection window.

### 4.1.6. Choosing models to calculate melt physical properties

Petrolog4 calculates melt density and viscosity during melt evolution. To choose from the available models, click on the blue text labels within the 'Melt physical properties' subsection of the Parameters Section (Figs. 1.1, 1.2, 2.2). Clicking on the blue text label next to 'Density:' opens the 'Density Models' pop-up window (Fig. 4.15). Chose the desired model by pressing on one of the radio buttons next to model names. The available models are listed in Appendix 1. Close the window by pressing the 'Ok' button. Pressing the 'Cancel' button closes the window without applying the changes made.

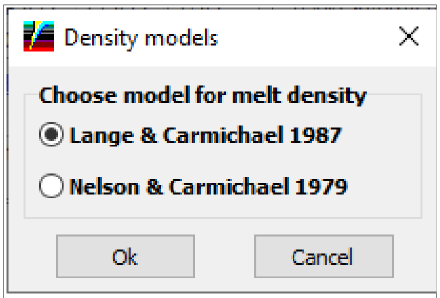



**Figure 4.15.** Window for choosing melt density models.

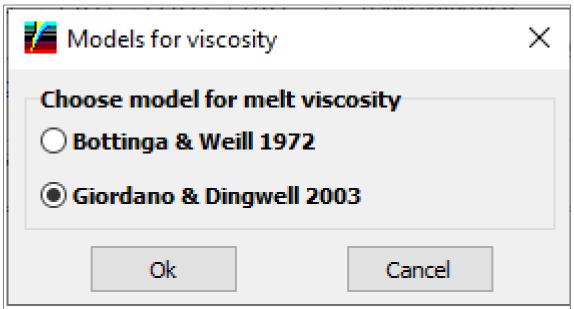



**Figure 4.16.** Window for choosing melt viscosity models.

Clicking on the blue text label next to 'Viscosity:' opens the 'Models for Viscosity' pop-up window (Fig. 4.16). Choose the desired model by pressing on one of the radio buttons next to model names. The available models are listed in Appendix 1. Close the window by pressing the 'Ok' button. Pressing the 'Cancel' button closes the window without applying the changes made.

### 4.1.7. Setting calculation step

A value for the calculation step is set in the 'Calculation step' text box inside the 'Calculation Parameters' sub-section in the Parameters Section (Figs. 1.1, 1.2, 2.2). The calculation step determines the amount (in wt.%) by which the melt mass decreases at each step of crystallisation calculations. The smaller the calculation step is the more precise the calculations are, but this also leads to the calculations taking longer. The default value of 0.01% of the amount of melt on each step provides acceptable precision and reasonably short calculation times. For implications of using larger or smaller crystallisation steps see Danyushevsky and Plechov, 2011. It is not recommended to increase the calculation step.

***Note:*** The algorithm used in Petrolog4 is designed with an assumption that the output of the intermediate states of the system during calculations would occur at frequencies which are at least 2 orders of magnitude larger than the calculation step. For example, if the calculation step is set to 0.01%, the smallest recommended output frequency is 1% of the extent of crystallisation.

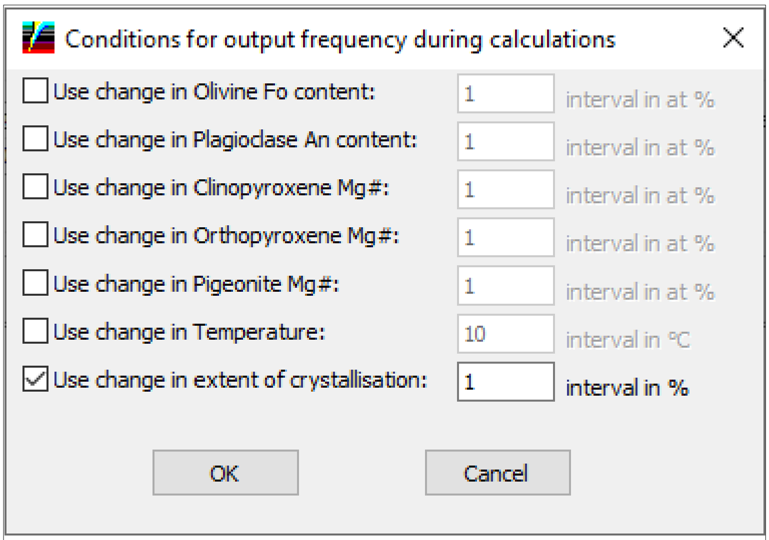



**Figure 4.17.** The 'Conditions for output frequency during calculations' window showing options available for setting conditions for the output of the intermediate states of the system during calculations.

### 4.1.8. Setting conditions for the frequency of results output during calculations

Petrolog4 offers several options for setting output frequency of the intermediate states of the system during calculations. The default setting is 1 wt.% of crystallisation. To change this setting, click on the blue text label below 'Define output frequency:' text label inside the 'Calculation Parameters' sub-section in the Parameters Section (Figs. 1.1, 1.2, 2.2). This will open the 'Conditions for output frequency during calculations' pop-up window (Fig. 4.17). Several options can be set simultaneously, and the program will report the intermediate states of the system satisfying all the selected criteria. The results are displayed in the Output Section of the Main Form (Fig. 1.2, see Section 4.1.9) and saved in several files (see Section 4.3).

Close the window by pressing the 'Ok' button. Pressing the 'Cancel' button closes the window without applying the changes made. The blue label will display the chosen option(s).

### 4.1.9. Output of results on screen during calculations

When calculations start, a summary of all calculations parameters is displayed (Table 4.1). If any volatile or trace elements are included in the starting composition, the summary includes a table with all distribution coefficients (Ds) that will be used during calculation.

***Note:*** If any of the volatile elements included in calculations are the major elements in some of the included phases (e.g., O in silicates and $H_2O$-$CO_2$ fluids, H and C in $H_2O$-$CO_2$ fluids, and reduced S in immiscible sulphide melts) their concentrations in the relevant phases will be determined using the chosen models of phase-melt equilibrium, and thus D values are not applicable to these elements in such phases (n/a) is listed in the table with Ds (see Table 4.1).

The summary of parameters is followed by the starting composition ('Start'; Table 4.2). If sulphur is present in the starting composition, the composition is checked for sulphide-oversaturation following the chosen model for sulphide saturation before calculations begin. If oversaturation is observed, the S concentration in the starting composition is adjusted to match sulphide saturation following the starting oxidation state. Similarly, if $H_2O$ and / or $CO_2$ are present in the starting composition, the composition is checked for fluid-oversaturation following the chosen model for fluid saturation before calculations begin. If oversaturation is observed, the $H_2O$ and / or $CO_2$ concentrations in the starting composition are adjusted to match fluid saturation at the starting pressure. A message stating the above is displayed above the starting composition (Table 4.2).

If the calculations are performed at the conditions of sulphide and /or fluid saturation, the concentrations of S, $H_2O$ and $CO_2$ are changed to reflect saturation following the chosen models for sulphide and /or fluid saturation. Messages stating the above are displayed above the starting composition (Table 4.2.). In the example shown in Table 4.2, the concentration of sulphur in the starting composition was above saturation at the chosen calculation parameters, and thus it has been reduced, whereas the concentrations of $H_2O$ and $CO_2$ where below saturation at the chosen parameters, and thus they were increased.

The composition that will be used as the starting composition ('Melt', see Table 4.2) is listed below the 'Start' composition. The default Petrolog4 output for chemical composition is using components for major and volatile elements (e.g., oxides for silicate and oxide minerals and $H_2O$-CO2 fluid, and mono-sulphides for an immiscible sulphide melt, see the upper section of Table 4.2). Reduced S is taken to be coupled to ferrous Fe in the melt phase, and thus its concentration in the melt is represented by the FeS component. Trace elements are displayed using elemental concentrations and the total amount of oxygen allocated to the trace elements is shown in the O_wt% column.

The user can choose to display results of calculations in elemental concentrations for all chemical elements (see lower section of Table 4.2). In this case, the O_wt% column would display the total O concentration and the Fe2 column will display the total ferrous Fe concentration. To switch between component and elemental outputs, use the 'Use Components for Screen Output' option (see Section 1.2).

Table 4.3 presents the state of the system after 2 % of crystallisation, i.e, when the mass of the melt is 98% of the starting mass, with other phases comprising 2 % of the initial mass of the starting melt. The first line of the output is the magma composition at the given stage of evolution. The magma composition represents the combined composition of the melt and all phases residing with the melt, i.e, the phases that are not fractionating from the melt. In the example used here, 20% of crystallising olivine would remain in the magma, 30 % of pyroxenes and 50% of plagioclase, fluid and immiscible sulphide melt (see Table 4.1).

The second line is the composition of the melt. When some proportions of the crystallising phases remain in the magma (as is the case for this example), the composition of the magma is different from the composition of the melt.

Below the melt are the compositions of all phases that are currently crystallising from the melt. In the example shown in Table 4.3, only olivine, fluid and sulphide phase have formed from the melt after 2% of crystallisation.

When components are used for the outputs, the compositions of fluid and sulphide melt are shown separately from other phases as the components in these two phases are different (see the upper section of Table 4.3). In the immiscible sulphide melt all major and trace elements are coupled with reduced sulphur. If oxygen is present, it is coupled with ferrous Fe forming the FeO component. Column 'S_ppm' displays the amount of sulphur coupled to trace elements. If H, C and oxidised sulphur are present in sulphide phase, they are coupled with oxygen.

In the fluid phase, reduced sulphur is coupled with hydrogen forming the $H_2S$ component, and oxidised sulphur is +4 rather than +6, thus forming the $SO_2$ component. When the results of calculations are displayed in elemental concentrations (see the lower section of Table 4.3), the value for each element in each phase displays the total elemental concentration in this phase.

***Note:*** When output using components is chosen, the magma composition in Table 4.3 is shown using the elemental concentrations. This is because when fluid and / or immiscible sulphide melt are present in the magma, it impossible to display the combined composition of all phases in the magma using components. When neither fluid nor sulphide are present in the magma, its composition is shown using components.

The phase compositions are followed by a line with phase compositional parameters of the crystallising phases (mol% forsterite (Fo) for Olivine; mol% anorthite (An) for Plagioclase; Mg# (100*Mg/(Mg+Fe)) for Clinopyroxene; Orthopyroxene; Pigeonite; Ilmenite and Magnetite; Cr# (100*Cr/(Cr+Al)) for Spinel; Fe# (100*Fe/(Ni+Fe)) for sulphide; CO2# (100*$CO_2$/($CO_2$+$H_2O$) in mol units) for fluid; Ca# (100*Ca/(Ca+Ba)) for sulphate; Si# (100*Si/(Si+Al)) for quartz; K# (100*K/(K+Na)) for orthoclase and leucite; Na# (100*Na/(K+Na)) for nepheline; Hf# (100*Hf/(Hf+Zr) for zircon; Ca# (100*Ca/(Ca+Sr+Ba+REE) for apatite.

The next line displays melt temperature, oxygen fugacity (as both an absolute value and a shift from the chosen reference buffer (Fig. 1.3)), and pseudo-liquidus temperatures for all minerals involved in calculations.

The next line contains weight proportions of all phases in the magma.

The next line shows crystallisation pressure, melt density and viscosity.

When some proportions of some of the phases fractionate from the magma (as is the case for the example in Tables 4.1, 4.2, 4.3), the compositions of fractionated phases are shown under the line with crystallisation pressure. The first line repeats component or element names. Below it, the composition of the combined fractionated phases called 'Cumulate' is displayed.

***Note:*** When fluid and / or immiscible sulphide melt are present among fractionated phases, the bulk composition of the 'Cumulate' is shown using elemental concentrations even if the output using component concentrations is chosen. This is because in such a case it is impossible to display the combined composition of fractionated phases (the 'Cumulate' composition) using components. When neither fluid nor sulphide are present, the composition of the 'Cumulate' is shown using components when the output using component concentrations is chosen.

Lines below the 'Cumulate' composition show bulk compositions of all fractionated phases at the given extent of melt evolution. The bulk compositions for each phase are calculated by mass-balancing fractionated compositions continuously formed during crystallisation.

***Note:*** To include the bulk composition of each phase in the cumulate in the output of results into files, use option Add export of cumulus phases to files' (see Section 1.2).

The next line below the bulk composition of each phase shows bulk fractionated phase compositional parameters. In most cases these will be higher (i.e., skewed towards the compositions of earlier formed crystals) than the compositions currently crystallising form the melt (see Danyushevsky and Plechov, 2011 for more details).

The last line of the output contains weight proportions of all phases in the cumulate.

Table 4.4 presents the state of the system after 40 % of crystallisation. At this extent of crystallisation, plagioclase and clinopyroxene joined the crystallising assemblage. Since plagioclase, fluid and sulphide are all set to fractionate at 50%, their amount in the magma and cumulate are equal, whereas there are larger amounts of olivine and clinopyroxene in the fractionated phases than in the magma since they were set to fractionate at 80% and 70%, respectively.

Table 4.1. Example output: Calculation parameters at the start of calculation

```
Modelling Crystallisation
Phases chosen for calculations are:
   Olv, Plg, Cpx, Opx, Pig, Slf, Fld, Sft
   The model used for Olv is: Herzberg & O'Hara 2002
    Olv fractionation is: 80.00 %
    The correction for the effect of H2O on Olv liquidus temperature is calculated using Petrolog default settings
   The model used for Plg is: Ariskin et al. 1993
    Fe content in plagioclase is calculated after Lundgaard & Tegner (2004)
    Plg fractionation is: 50.00 %
    The correction for the effect of H2O on Plg liquidus temperature is calculated using Petrolog default settings
   The model used for Cpx is: Ariskin et al. 1993
    Cpx fractionation is: 70.00 %
    The correction for the effect of H2O on Cpx liquidus temperature is calculated using Petrolog default settings
   The model used for Opx is: Bolikhovskaya et al. 1996
    Opx fractionation is: 70.00 %
    The correction for the effect of H2O on Opx liquidus temperature is calculated using Petrolog default settings
   The model used for Pig is: Bolikhovskaya et al. 1996
    Pig fractionation is: 70.00 %
    The correction for the effect of H2O on Pig liquidus temperature is calculated using Petrolog default settings
   The model used for Slf is: Kiseeva & Wood 2015
    Slf fractionation is: 50.00 %
    The correction for the effect of H2O on Slf liquidus temperature is calculated using Petrolog default settings
   The model used for Fld is: Iacono-Marziano et al 2012
    Fld fractionation is: 50.00 %
   The model used for Sft is: Ca sulphate
    Sft fractionation is: 50.00 %
    The correction for the effect of H2O on Sft liquidus temperature is calculated using Petrolog default settings
Fe2O3 in the melt is calculated using an assumption of closed system for oxygen
   f(O2) is calculated following the model of Borisov et al 2018
Sulfur speciation in the melt is calculated using the model of O'Neill & Mavrogenes 2022
Calculations are performed assuming fluid saturation
Fluid saturation of the melt is calculated using the model of Iacono-Marziano et al 2012
Calculations are performed assuming sulfide saturation
Sulfide saturation of the melt is calculated using the model of O'Neill 2021
Sulfate saturation of the melt is calculated using the model of Zajacz & Tsay 2019
Initial Pressure = 5 kbar
   During calculations Pressure is changed at 20 % crystallisation to 3 kbars
                                           at 25 % crystallisation to 2 kbars
                                           at 35 % crystallisation to 1 kbars
                                           at 50 % crystallisation to 0 kbars
Melt density is calculated following the model of Lange & Carmichael 1987
Melt viscosity is calculated following the model of Giordano & Dingwell 2003
Parameters to stop calculations at:
   Final degree of fractionation: 70 %
The amount of a mineral phase which will be extracted from
   100% of melt on each step is:    0.01 %
Ds for phases:
```

| Mineral | H | C+ | S- | S+ | O | Co | Ni | Cu | Rb | Sr | Ba | Yb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Olv | 0 | 0 | 0 | 0 | n/a | Beatt91 | Herzb02 | 0 | 0.001 | 0.01 | 0 | 0 |
| Plg | 0 | 0 | 0 | 0 | n/a | 0 | 0 | 0 | 0.1 | Bl_Wo91 | Bl_Wo91 | 0 |
| Cpx | 0 | 0 | 0 | 0 | n/a | 0.2 | 1 | 0 | 0.05 | 0.07 | 0.03 | Wo_Bl97 |
| Opx | 0 | 0 | 0 | 0 | n/a | 0.8 | 1.5 | 0 | 0.02 | 0.05 | 0.015 | 0 |
| Pig | 0 | 0 | 0 | 0 | n/a | 0.8 | 1.2 | 0 | 0.03 | 0.05 | 0.02 | 0 |
| Slf | 0 | 0 | n/a | 0 | KiWd2015 | KiWd2015 | KiWd2015 | KiWd2015 | 0 | 0 | 0 | 0 |
| Fld | n/a | n/a | Ding2023 | Ding2023 | n/a | 0 | 0 | 0 | 0.2 | 0.1 | 0.3 | 0 |
| Sft | 0 | 0 | 0 | n/a | n/a | 0 | 0 | 0 | 0 | 0 | 1.5 | 0 |

------------------------------------------------------------------------------------------------------------------------------------------

Table 4.2. Example output: The starting composition

Output using component concentrations

The starting composition "Analysis2" has been adjusted for the chosen oxidation state, checked for fluid and sulfide saturation, and recalculated to 100 wt%

Since "Fluid saturated" option is selected, H2O and/or CO2 contents in the starting composition have been adjusted to match fluid saturation.
Since "Sulfide saturated" option is selected, S content in the starting composition has been adjusted to match sulfide saturation.

| | SiO2 | TiO2 | Al2O3 | Fe2O3 | FeO | MnO | MgO | CaO | Na2O | K2O | P2O5 | Cr2O3 | FeS*_ppm | H2O_wt% | CO2_ppm | S_ppm | SO3_ppm | O_wt% | Co_ppm | Ni_ppm | Cu_ppm | Rb_ppm | Sr_ppm | Ba_ppm | Yb_ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Start | 51.00 | 1.30 | 16.00 | 1.00 | 7.78 | 0.18 | 11.00 | 10.00 | 1.70 | 0.70 | 0.11 | 0.11 | 2742.0 | 0.500 | 3000.0 | | 0.0 | 0.011 | 55.0 | 200.0 | 150.0 | 9.0 | 86.0 | 3.0 | 10.0 |
| Melt | 49.96 | 1.27 | 15.67 | 0.98 | 7.65 | 0.18 | 10.78 | 9.80 | 1.67 | 0.69 | 0.11 | 0.11 | 2289.6 | 0.515 | 3414.7 | | 2.2 | 0.010 | 53.9 | 195.9 | 146.9 | 8.8 | 84.2 | 2.9 | 9.8 |

Output using elemental components

The starting composition "Analysis2" has been adjusted for the chosen oxidation state, checked for fluid and sulfide saturation, and recalculated to 100 wt%

Since "Fluid saturated" option is selected, H2O and/or CO2 contents in the starting composition have been adjusted to match fluid saturation.
Since "Sulfide saturated" option is selected, S content in the starting composition has been adjusted to match sulfide saturation.

| | Si | Ti | Al | Fe3 | Fe2 | Mn | Mg | Ca | Na | K | P | Cr | H_ppm | C+_ppm | S-_ppm | S+_ppm | O_wt% | Co_ppm | Ni_ppm | Cu_ppm | Rb_ppm | Sr_ppm | Ba_ppm | Yb_ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Start | 23.84 | 0.78 | 8.47 | 0.70 | 6.22 | 0.14 | 6.63 | 7.15 | 1.26 | 0.58 | 0.05 | 0.08 | 555.6 | 818.7 | 1000.0 | 0.0 | 45.832 | 55.0 | 200.0 | 150.0 | 9.0 | 86.0 | 3.0 | 10.0 |
| Melt | 23.36 | 0.76 | 8.30 | 0.69 | 6.09 | 0.14 | 6.50 | 7.00 | 1.24 | 0.57 | 0.05 | 0.07 | 571.7 | 931.8 | 835.0 | 0.9 | 44.963 | 53.9 | 195.9 | 146.9 | 8.8 | 84.2 | 2.9 | 9.8 |

***Note:*** When components are used for output and the starting composition does not contain any trace or volatile elements except O, the O_wt% column is not displayed.

***Note:*** When components are used for output and the starting composition does not contain any trace elements but contains volatile elements in addition to O, the O_wt% column displays a 0 value.

***Note:*** When components are used for output and the starting composition does not contain sulphur, the FeS*_ppm, S_ppm and SO3_ppm columns are not displayed

***Note:*** '*' in the name of the FeS*_ppm column indicates that if reduced sulphur is present at a trace level in plagioclase or nepheline, it is coupled to Na and this column would display the concentration of $Na_2S$ in ppm; if reduced sulphur is present at a trace level in orthoclase or leucite, it is coupled to K and this column would display the concentration of $K_2S$ in ppm; if reduced sulphur is present at a trace level in quartz, it is coupled to Si and this column would display the concentration of $SiS_2$ in ppm; if reduced sulphur is present at a trace level in sulphate, it is coupled to Ca and this column would display the concentration of CaS in ppm.

Table 4.3. Example output: An intermediate state of the system during calculations at 2% of crystallisation of the starting composition (Tables 4.1, 4.2)

<u>Output using component concentrations</u>

```
             Si    Ti    Al   Fe3   Fe2    Mn    Mg    Ca    Na     K     P    Cr    H_ppm   C+_ppm   S-_ppm   S+_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Magma     23.43  0.78  8.43  0.70  6.05  0.14  6.15  7.11  1.26  0.58  0.05  0.07    580.9    899.5    837.8      1.3   44.989     52.0    162.2    145.0      9.0     85.6      3.0     10.0
           SiO2  TiO2 Al2O3 Fe2O3   FeO   MnO   MgO   CaO  Na2O   K2O  P2O5 Cr2O3 FeS*_ppm  H2O_wt%  CO2_ppm    S_ppm  SO3_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Melt      50.17  1.30 15.99  1.00  7.58  0.18 10.05  9.99  1.70  0.70  0.11  0.11   2279.0    0.525   3135.6               2.9    0.009     51.5    150.1    141.0      9.0     85.9      3.0     10.0
Olv       40.33  0.04  0.11  0.00 11.46  0.20 47.28  0.29  0.00  0.00        0.04                                                 0.052    168.4   1746.0               0.0      0.9
           SiO2  TiO2 Al2O3 Fe2O3   FeO   MnO   MgO   CaO  Na2O   K2O  P2O5 Cr2O3           H2O_wt%  CO2_ppm  H2S_ppm  SO2_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Fld                                                                                      0.384 994615.0    106.6   1421.1    0.000                                 1.8      8.6      0.9
           SiS2  TiS2 Al2S3 Fe2S3   FeS   MnS   MgS   CaS  Na2S   K2S  P2S5 Cr2S3  FeO_ppm  H2O_wt%  CO2_ppm    S_ppm  SO3_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Slf                               49.57                                            45037.9                   135406.4                     2612.2 180124.9 141095.4
Fo= 88.025 Kd(Olv-Melt)= 0.314; Fe#Slf= 67.122; CO2#Fl= 99.064;
T=1213.3 (Olv); Lg(fO2)=-8.52 dQFM=-0.73; TPlg=1115.8 TCpx=1154.9 TOpx=1191.4 TPig=1167.7 TMgt=975.4
Amounts (wt%) of phases in magma: Melt 97.9991; Olv 0.3920; Slf 0.0032; Fld 0.01718;
Pressure: 4.800 kbar; Density: 2.677 g/cm3;  Viscosity: v=26 poise; ln(v)=3.2
             Si    Ti    Al   Fe3   Fe2    Mn    Mg    Ca    Na     K     P    Cr    H_ppm   C+_ppm   S-_ppm   S+_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Cumulate  18.63  0.03  0.06  0.00  8.69  0.15 28.26  0.20  0.00  0.00        0.03      4.4   2937.3    631.8      6.7   43.337    169.4   2287.1    269.7      0.0      0.9      0.0
           SiO2  TiO2 Al2O3 Fe2O3   FeO   MnO   MgO   CaO  Na2O   K2O  P2O5 Cr2O3 FeS*_ppm  H2O_wt%  CO2_ppm    S_ppm  SO3_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Olv       40.37  0.04  0.11  0.00 11.23  0.20 47.46  0.28  0.00  0.00        0.04                                                 0.057    166.4   1920.3               0.0      0.9
           SiO2  TiO2 Al2O3 Fe2O3   FeO   MnO   MgO   CaO  Na2O   K2O  P2O5 Cr2O3           H2O_wt%  CO2_ppm  H2S_ppm  SO2_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Fld                                                                                      0.361 995028.9    101.2   1245.2    0.000                                 1.8      8.5      0.9
           SiS2  TiS2 Al2S3 Fe2S3   FeS   MnS   MgS   CaS  Na2S   K2S  P2S5 Cr2S3  FeO_ppm  H2O_wt%  CO2_ppm    S_ppm  SO3_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Slf                               47.85                                            42224.4                   143475.4                     2567.1 197311.3 135962.6
Fo= 88.277; Fe#Slf= 64.205; CO2#Fl= 98.231;
Amounts (wt%) of cumulate phases: Olv 1.5682; Slf 0.0032; Fld 0.01718;
------------------------------------------------------------------------------------------------------------------------
```

<u>Output using elemental concentrations</u>

```
             Si    Ti    Al   Fe3   Fe2    Mn    Mg    Ca    Na     K     P    Cr    H_ppm   C+_ppm   S-_ppm   S+_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Magma     23.43  0.78  8.43  0.70  6.05  0.14  6.15  7.11  1.26  0.58  0.05  0.07    580.9    899.5    837.8      1.3   44.989     52.0    162.2    145.0      9.0     85.6      3.0     10.0
Melt      23.45  0.78  8.46  0.70  6.04  0.14  6.06  7.14  1.26  0.58  0.05  0.07    583.3    855.7    831.1      1.2   44.993     51.5    150.1    141.0      9.0     85.9      3.0     10.0
Olv       18.85  0.03  0.06  0.00  8.91  0.16 28.51  0.21  0.00  0.00        0.03                                     43.057    168.4   1746.0               0.0      0.9
Slf                               34.99                                                               316192.3              1.003   2612.2 180124.9 141095.4
Fld                                                                               433.4 271423.0    100.3    711.2   72.732                                 1.8      8.6      0.9
Fo= 88.025 Kd(Olv-Melt)= 0.314; Fe#Slf= 67.122; CO2#Fl= 99.064;
T=1213.3 (Olv); Lg(fO2)=-8.52 dQFM=-0.73; TPlg=1115.8 TCpx=1154.9 TOpx=1191.4 TPig=1167.7
Amounts (wt%) of phases in magma: Melt 97.9991; Olv 0.3920; Slf 0.0032; Fld 0.01718;
Pressure: 4.800 kbar; Density: 2.677 g/cm3;  Viscosity: v=26 poise; ln(v)=3.2
             Si    Ti    Al   Fe3   Fe2    Mn    Mg    Ca    Na     K     P    Cr    H_ppm   C+_ppm   S-_ppm   S+_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Cumulate  18.63  0.03  0.06  0.00  8.69  0.15 28.26  0.20  0.00  0.00        0.03      4.4   2937.3    631.8      6.7   43.337    169.4   2287.1    269.7      0.0      0.9      0.0
Olv       18.87  0.03  0.06  0.00  8.73  0.15 28.62  0.20  0.00  0.00        0.03                                     43.100    166.4   1920.3               0.0      0.9
Slf                               33.68                                                               317965.2              0.940   2567.1 197311.3 135962.6
Fld                                                                               407.2 271535.9     95.3    623.2   72.733                                 1.8      8.5      0.9
Fo= 88.277; Fe#Slf= 64.205; CO2#Fl= 98.231;
Amounts (wt%) of cumulate phases: Olv 1.5682; Slf 0.0032; Fld 0.01718;
```

***Note:*** When output using components is chosen, the magma composition in this example is shown using the elemental concentration. This is because when fluid and / or immiscible sulphide melt are present in the magma, it impossible to display the combined composition of all phases in the magma using components. When neither fluid nor sulphide are present in the magma, its composition is shown using components.

***Note:*** When fluid and / or immiscible sulphide melt are present among fractionated phases, the bulk composition of the 'Cumulate' is shown using elemental concentration even if the output using component concentrations is chosen. This is because in such a case it is impossible to display the combined composition of fractionated phases (the 'Cumulate' composition) using components. When neither fluid nor sulphide are present, the composition of the 'Cumulate' is shown using components when the output using component concentrations is chosen.

Table 4.4. Example output: An intermediate state of the system during calculations at 40% of crystallisation of the starting composition (Tables 4.1, 4.2)

## Output using component concentrations

```
             Si    Ti    Al   Fe3   Fe2    Mn    Mg    Ca    Na     K     P    Cr    H_ppm   C+_ppm   S-_ppm   S+_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Magma     24.29  1.02  8.68  0.87  6.20  0.15  3.80  7.17  1.45  0.76  0.06  0.09    764.6    629.1    891.5     18.2   45.168     41.3     42.4    105.8     11.7     94.2      3.9     12.7
           SiO2  TiO2 Al2O3 Fe2O3   FeO   MnO   MgO   CaO  Na2O   K2O  P2O5 Cr2O3 FeS*_ppm  H2O_wt%  CO2_ppm    S_ppm  SO3_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Melt      53.29  2.11 14.99  1.49  8.50  0.22  5.32  9.48  1.99  1.14  0.18  0.16   2300.2    0.831    249.4              21.1    0.004     37.8     13.1     49.2     14.2     90.1      4.6     15.5
Plg       49.07       32.34  0.35  0.22             15.25  2.76                                                                   0.003                                 1.4    164.8      0.9
Olv       39.02  0.07  0.11  0.00 18.16  0.40 41.66  0.41  0.00  0.00        0.10                                                 0.014    216.0    286.5               0.0      0.9
Cpx       50.93        6.05        8.20       16.11 18.71                                                                         0.001      7.6     13.2               0.7      6.3      0.1     10.6
           SiO2  TiO2 Al2O3 Fe2O3   FeO   MnO   MgO   CaO  Na2O   K2O  P2O5 Cr2O3            H2O_wt%  CO2_ppm  H2S_ppm  SO2_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Fld                                                                                          8.012 907600.3   2454.7   9805.0    0.000                                 2.8      9.0      1.4
           SiS2  TiS2 Al2S3 Fe2S3   FeS   MnS   MgS   CaS  Na2S   K2S  P2S5 Cr2S3  FeO_ppm  H2O_wt%  CO2_ppm    S_ppm  SO3_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Slf                               74.19                                           84027.7                    42756.0                     2895.3  29855.5  98603.6
An= 75.351; Fo= 80.349 Kd(Olv-Melt)= 0.267; Mg#Cpx= 77.787; Fe#Slf= 94.972; CO2#Fl= 82.247;
T=1058.0 (Plg); Lg(fO2)=-9.75 dQFM=0.31; TOlv=1058.0 TCpx=1058.0 TOpx=1040.1 TPig=1047.3 TMgt=988.0
Amounts (wt%) of phases in magma: Melt 59.9944; Olv 2.9942; Plg 9.6513; Cpx 1.5860; Slf 0.0499; Fld 0.17262;
Pressure: 0.666 kbar; Density: 2.666 g/cm3;  Viscosity: v=60 poise; ln(v)=4.1
             Si    Ti    Al   Fe3   Fe2    Mn    Mg    Ca    Na     K     P    Cr    H_ppm   C+_ppm   S-_ppm   S+_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Cumulate  20.63  0.01  7.16  0.08  5.83  0.09 14.35  6.51  0.60  0.00        0.02      9.7   1813.9    610.3     10.4   44.364     90.6    643.2    266.9      0.5     55.3      0.3      1.4
           SiO2  TiO2 Al2O3 Fe2O3   FeO   MnO   MgO   CaO  Na2O   K2O  P2O5 Cr2O3 FeS*_ppm  H2O_wt%  CO2_ppm    S_ppm  SO3_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Olv       39.98  0.05  0.10  0.00 13.34  0.25 45.73  0.35  0.00  0.00        0.06                                                 0.033    179.5   1029.9               0.0      0.9
Plg       47.73       33.30  0.29  0.19             16.34  2.13                                                                   0.003                                 1.1    142.7      0.6
Cpx       50.92        6.30        7.36       16.27 19.14                                                                         0.001      7.5     15.8               0.7      6.3      0.1      9.4
           SiO2  TiO2 Al2O3 Fe2O3   FeO   MnO   MgO   CaO  Na2O   K2O  P2O5 Cr2O3            H2O_wt%  CO2_ppm  H2S_ppm  SO2_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Fld                                                                                          1.267 983880.0    364.2   3076.7    0.000                                 2.1      9.0      1.0
           SiS2  TiS2 Al2S3 Fe2S3   FeS   MnS   MgS   CaS  Na2S   K2S  P2S5 Cr2S3  FeO_ppm  H2O_wt%  CO2_ppm    S_ppm  SO3_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Slf                               63.32                                           66424.2                    80139.5                     2757.9  80910.5 136539.1
Fo= 85.939; An= 80.922; Mg#Cpx= 79.763; Fe#Slf= 85.498; CO2#Fl= 93.993;
Amounts (wt%) of cumulate phases: Olv 11.9769; Plg 9.6513; Cpx 3.7007; Slf 0.0499; Fld 0.17262;
------------------------------------------------------------------------------------------------------------------------
```

## Output using elemental concentrations

```
             Si    Ti    Al   Fe3   Fe2    Mn    Mg    Ca    Na     K     P    Cr    H_ppm   C+_ppm   S-_ppm   S+_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Magma     24.29  1.02  8.68  0.87  6.20  0.15  3.80  7.17  1.45  0.76  0.06  0.09    764.6    629.1    891.5     18.2   45.168     41.3     42.4    105.8     11.7     94.2      3.9     12.7
Melt      24.91  1.26  7.93  1.04  6.75  0.17  3.21  6.78  1.48  0.95  0.08  0.11    922.8     68.0    838.9      8.4   45.113     37.8     13.1     49.2     14.2     90.1      4.6     15.5
Plg       22.94       17.11  0.25  0.17             10.90  2.04                                                          46.574                                 1.4    164.8      0.9
Olv       18.24  0.04  0.06  0.00 14.12  0.31 25.13  0.30  0.00  0.00        0.07                                        41.695    216.0    286.5               0.0      0.9
Cpx       23.81        3.20        6.38        9.72 13.37                                                                43.527      7.6     13.2               0.7      6.3      0.1     10.6
Slf                               53.66                                                             313306.5              1.871   2895.3  29855.5  98603.6
Fld                                                                                  9046.9 247677.3   2310.5   4907.1   73.604                                 2.8      9.0      1.4
An= 75.351; Fo= 80.349 Kd(Olv-Melt)= 0.267; Mg#Cpx= 77.787; Fe#Slf= 94.972; CO2#Fl= 82.247;
T=1058.0 (Plg); Lg(fO2)=-9.75 dQFM=0.31; TOlv=1058.0 TCpx=1058.0 TOpx=1040.1 TPig=1047.3 TMgt=988.0
Amounts (wt%) of phases in magma: Melt 59.9944; Olv 2.9942; Plg 9.6513; Cpx 1.5860; Slf 0.0499; Fld 0.17262;
Pressure: 0.666 kbar; Density: 2.666 g/cm3;  Viscosity: v=60 poise; ln(v)=4.1
             Si    Ti    Al   Fe3   Fe2    Mn    Mg    Ca    Na     K     P    Cr    H_ppm   C+_ppm   S-_ppm   S+_ppm    O_wt%   Co_ppm   Ni_ppm   Cu_ppm   Rb_ppm   Sr_ppm   Ba_ppm   Yb_ppm
Cumulate  20.63  0.01  7.16  0.08  5.83  0.09 14.35  6.51  0.60  0.00        0.02      9.7   1813.9    610.3     10.4   44.364     90.6    643.2    266.9      0.5     55.3      0.3      1.4
Olv       18.69  0.03  0.05  0.00 10.37  0.19 27.58  0.25  0.00  0.00        0.04                                        42.683    179.5   1029.9               0.0      0.9
Plg       22.31       17.62  0.20  0.15             11.68  1.58                                                          46.440                                 1.1    142.7      0.6
Cpx       23.81        3.33        5.72        9.81 13.68                                                                43.643      7.5     15.8               0.7      6.3      0.1      9.4
Slf                               45.39                                                             311072.5              1.479   2757.9  80910.5 136539.1
Fld                                                                                  1428.6 268493.5    342.8   1539.8   72.818                                 2.1      9.0      1.0
Fo= 85.939; An= 80.922; Mg#Cpx= 79.763; Fe#Slf= 85.498; CO2#Fl= 93.993;
Amounts (wt%) of cumulate phases: Olv 11.9769; Plg 9.6513; Cpx 3.7007; Slf 0.0499; Fld 0.17262;
```

### 4.1.10. Setting conditions to stop calculations

Petrolog4 offers several options for defining conditions for stopping calculations. The default setting is 0 wt.% of crystallisation, indicating that no crystallisation calculation is performed. To change this setting, click on the blue text label below 'Define conditions to stop calculations:' text label inside the 'Calculation Parameters' sub-section in the Parameters Section (Figs. 1.1, 1.2, 2.2). The 'Conditions for stopping calculations' window will pop-up (Fig. 4.18). The user must choose one of the available options.

Close the window by pressing the 'Ok' button. Pressing the 'Cancel' button closes the window without applying the changes made. The blue label will display the chosen option.

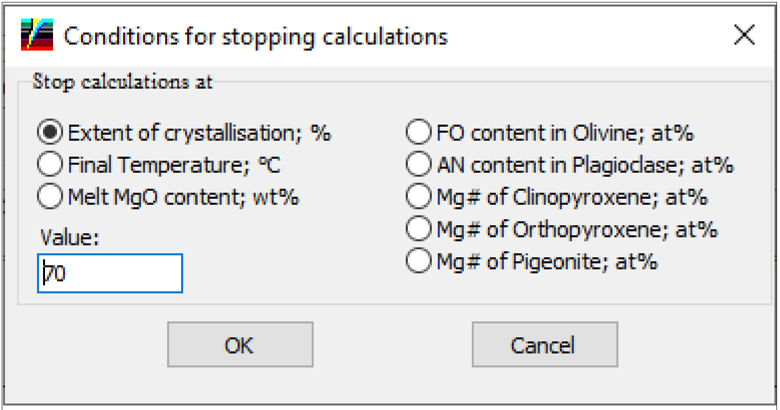



**Figure 4.18.** The 'Conditions for stopping calculation' window showing options available for setting conditions for stopping calculations.

***Note:*** The data file can contain columns that contain conditions to stop calculations that can differ for each analysis. Such columns should have the following name in the header row: LASTFRAC or LAST_FRAC, LASTTEMP or LAST_TEMP, LASTMGO or LAST_MGO, LASTFO or LAST_FO, LASTAN or LAST_AN, LASTCPX or LAST_CPX, LASTOPX or LAST_OPX, LASTPIG or LAST_PIG corresponding to the options shown on Fig. 4.18. The parameters should be in the same units as shown on Fig. 4.18.

### 4.1.11. Setting conditions for modelling replenishment

Petrolog4 algorithm allows for modelling replenishment of the crystallising system by the parental melt during pure fractional crystallisation. Replenishment involves repeated instances of recharge of the crystallising system by the parental melt (i.e., by a melt of the same composition as the starting composition), and optional linked instances of eruptions of the evolved melt from the crystallising system. When Petrolog4 starts, replenishment is not chosen. To set replenishment parameters click on one of the three blue labels ('Recharge…', 'Eruption…' or 'Trigger…') in the 'Replenishment parameters' subsection of the Parameters Section of the Main form (Figs. 1.1, 1.2, 2.2).

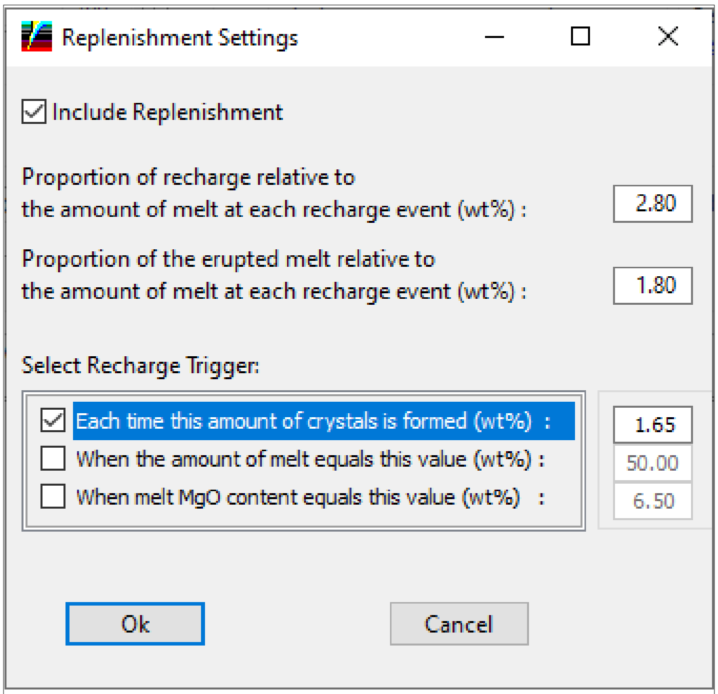



**Figure 4.19.** The 'Replenishment Settings' window showing options available for setting conditions for the primitive melt recharge and evolved melt eruption during calculations.

Clicking on any of the three blue labels opens the Replenishment Settings form (Fig. 4.19).

***Note:*** Since replenishment is only enabled for the case of pure fractional crystallisation, if the extent of fractionation is set to less than 100 for any of the phases (see section 4.1.2), the 'Replenishment parameters' subsection is disabled (Fig. 1.2).

The mass of the recharge and eruption events is set separately as a percentage of the mass of the melt present in the crystallising system. (Fig. 4.19). If the percentage of the erupted melt is lower than the recharge, the mass of the crystallising system increases with each recharge. Conversely, if the mass of the erupted melt exceeds the mass of the recharge, the mass of the crystallising system continuously decreases during calculations. Petrolog4 algorithm places eruption events immediately prior to recharge events, i.e., there is always the same number of eruption and recharge events.

To enable replenishment calculations, the user also needs to specify the trigger for recharge evants (Fig. 4.19). Petrolog4 offers a choice of three triggers:
1) when a specified proportion of crystals is formed after the beginning of calculations or after the pervious recharge instance. This trigger option allows the composition of the melt inside the crystallising system to continuously evolve towards more fractionated compositions;
2) when the proportion of melt in the crystallising system reaches a set value. Using this trigger requires that the proportion of recharge is larger than the proportion of the erupted melt. This trigger will maintain the proportion of melt in the crystallising system near the set value, resulting a steady-state-like scenario when the major element compositions of the erupted melts will be similar;
3) when the MgO content in the melt reaches a set value. In most cases this trigger requires that the set value for the MgO content in the melt is lower than the MgO content in the starting composition. Similarly to the second trigger, a steady-state-like scenario will occur resulting in similar major element compositions of the erupted melts.

When replenishment is included in calculations, each recharge event triggers output of the state of the system immediately after the recharge, and the composition of the erupted melt is recorded immediately prior to recharge. Petrolog4 output contains values for the number of recharge events that occurred from the beginning of calculation; the current mass of the crystallising system relative to the initial mass; the current mass of the erupted melt relative to the initial mass, and the current mass of recharge relative to the initial mass.

### *4.2. Saving and loading calculation parameters*

To save the current set of calculation parameters, use the 'Save Parameters' option in the 'File' section of the Main Menu on the Main form (Fig. 2.2). In the dialog form that appears, enter a file name and press Save.

***Note:*** Petrolog4 assigns .PtlParam extension to files with parameter values.

Petrolog4 offers options to include the names of either the data file or the file with the saved D values, or both, in the parameters file. To set these two options, use the 'Petrolog Options' form that is opened by choosing the 'Options' item in the 'Tools' section of the Main Menu (Fig. 2.4)

***Note:*** When planning to pass on files with parameters to other users, before saving the parameters file, deselect options for including the names of the data file and the file with the saved D values in the parameters file.

To load a previously saved set of calculation parameters, use the 'Load Parameters' option in the 'File' section of the Main Menu on the Main form (Fig. 2.2). Chose the file in the dialog window and press Open.

#### 4.2.1. Saving the Default Set of calculation parameters.

To save the current set of calculation parameters as the Default Set, use the 'Save Parameters as the Default Set' option in the 'File' section of the Main Menu on the Main form (Fig. 2.2). Once saved, this set of parameters will be loaded every time Petrolog4 starts. To reload this set of parameters while using Petrolog4, use 'Load the Default Set of Parameters' option in the 'File' section of the Main Menu on the Main form (Fig. 2.2).

***Note:*** The Program Default set of parameters can be restored by using the 'Reset Program Defaults' option of the Tools Menu (Fig. 1.2).

### *4.3. Structure of output files*

During modelling of crystallisation, Petrolog4 saves the following files:

FileName_FRAC___calc_param.csv file lists values of all calculation parameters.

FileName_FRAC__.csv file contains:
magma, melt and bulk cumulate compositions;
proportions of all phases in the magma and cumulate;

compositional parameters of phases crystallising from the magma;
compositional parameters of the bulk phases in the cumulate;
temperature, pressure and melt physical properties.

Compositions of each phase in equilibrium with the melt at each recorded stage of fractionation are saved in a separate file. Such files have the following names:
FileName_FRAC_Olv_MAG.csv for olivine compositions;
FileName_FRAC_Plg_MAG.csv for plagioclase compositions;
FileName_FRAC_Cpx_MAG.csv for clinopyroxene compositions;
FileName_FRAC_Opx_MAG.csv for orthopyroxene compositions;
FileName_FRAC_Pig_MAG.csv for pigeonite compositions;
FileName_FRAC_Spl_MAG.csv for spinel compositions;
FileName_FRAC_Ilm_MAG.csv for ilmenite compositions;
FileName_FRAC_Mgt_MAG.csv for magnetite compositions;
FileName_FRAC_Slf_MAG.csv for sulphide compositions;
FileName_FRAC_Fld_MAG.csv for fluid compositions;
FileName_FRAC_Qtz_MAG.csv for quartz compositions;.
FileName_FRAC_Ort_MAG.csv for orthoclase compositions;
FileName_FRAC_Nph_MAG.csv for nepheline compositions;
FileName_FRAC_Lct_MAG.csv for leucite compositions.
FileName_FRAC_Zrn_MAG.csv for zircon compositions.
FileName_FRAC_Erupt_Melt.csv for compositions of the erupted melt.

***Note:*** When 'Add export of elemental concentrations to files' option is used (see Section 1.2), an additional set of files with phase compositions will be add that have '_EL' added at the end of their names (e.g., FileName_FRAC__EL.csv, FileName_FRAC_Plg_MAG_EL.csv, etc.).

***Note:*** When 'Add export of cumulus phases to files' option is used (see Section 1.2), an additional set of files with phase compositions will be add that have '_CUM' added at the end of their names instead of 'MAG' (e.g., FileName_FRAC_Plg_CUM.csv, FileName_FRAC_Plg_CUM_EL.csv, etc.).

***Note:*** File that are saved during each calculation are only for those phases that have appeared on the liquidus during calculations.

***Note:*** When exporting results of previous calculations to Excel, the user *must* click on the FileName_FRAC__.csv file to initiate export.

***Note:*** When using user-defined file names, it is recommended to keep file names under 15 characters long, since the length of allowed names for individual sheets in Excel files is limited to 31 characters.

# 5. Melt liquidus association

To determine melt liquidus association, choose ‘Melt liquidus association’ tab of the Main form (Fig. 5.1).

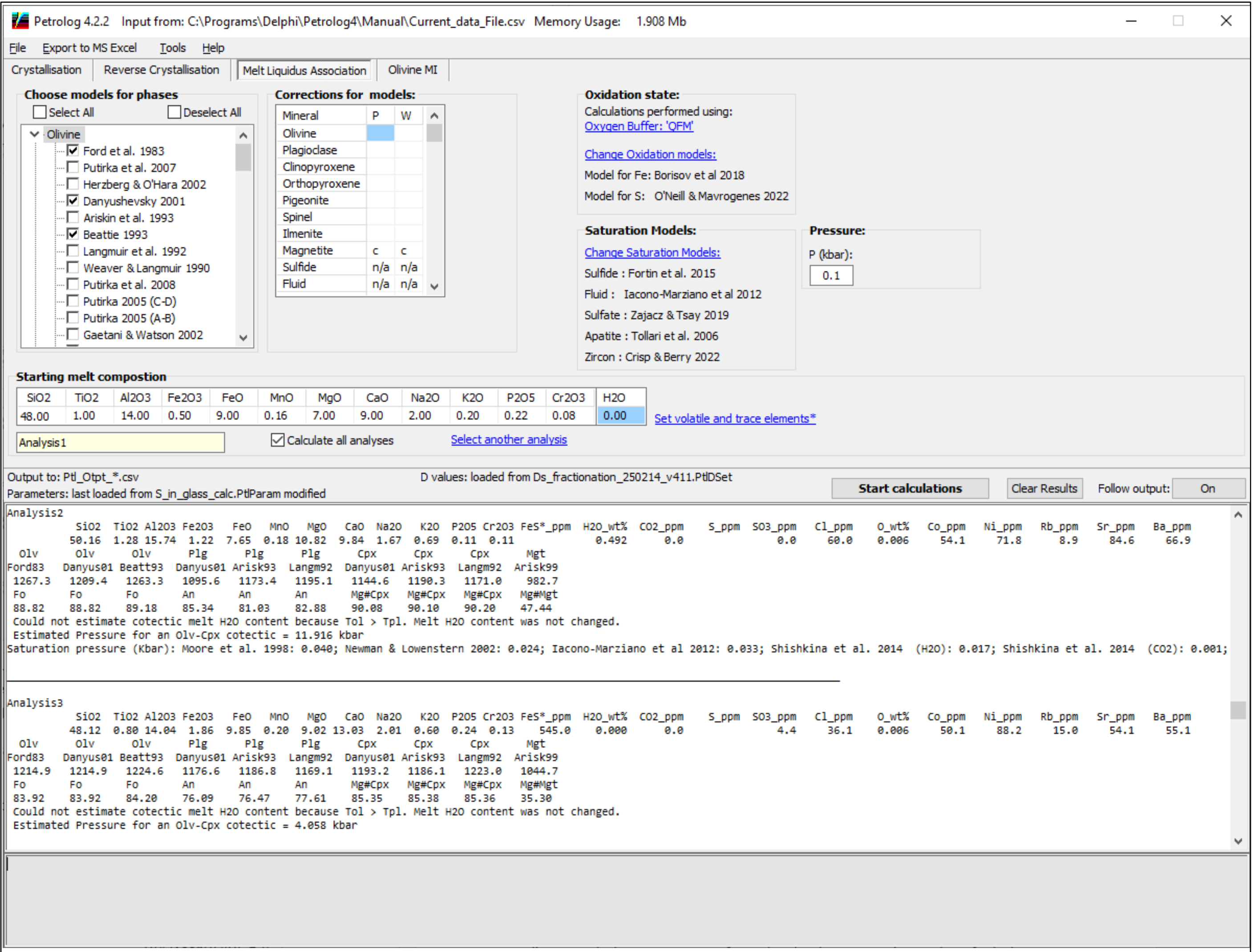



**Figure 5.1.** ‘Melt Liquidus Association’ option of Petrolog4 interface.

***Note:*** It is recommended that you read Section 4 of this manual before reading this section.

In this option, Petrolog4 does not model a crystallisation path but calculates pseudo-liquidus temperatures and liquidus phase compositions for a chosen set of phases and phase-melt equilibrium models. The following phase compositional parameters are also calculated:

| | |
|---|---|
| Olivine: | mol% forsterite (Fo); |
| Plagioclase: | mol% anorthite (An); |
| Clinopyroxene; Orthopyroxene; Pigeonite; Ilmenite and Magnetite: | Mg# (100*Mg/(Mg+Fe)); |
| Spinel: | Cr# (100*Cr/(Cr+Al)); |
| Sulphide: | Fe# (100*Fe/(Fe+Ni)); |
| Fluid (mol units): | CO2# (100*$CO_2$/($CO_2$+$H_2O$)). |
| Sulphate: | Ca# (100*Ca/(Ca+Ba)); |
| Quartz: | Si# (100*Si/(Si+Al)); |
| Orthoclase; Leucite: | K# (100*K/(K+Na)); |
| Nepheline: | Na# (100*Na/(K+Na)); |
| Zircon: | Hf# (100*Hf/(Hf+Zr)); |
| Apatite: | Ca# (100*Ca/(Ca+Sr+Ba+REE). |

By comparing calculated temperatures for different phases, the liquidus association of a melt composition can be established according to the chosen phase-melt equilibrium models. As the stated errors for most models are ~ 15 - 20 °C, the liquidus association would include the phase(s) with the highest calculated temperature (i.e., the liquidus temperature) and phases which pseudo-liquidus temperatures are within ~ 20 °C of the calculated liquidus temperature.

***Note:*** During melt liquidus association calculations it is possible to choose any number of models for each phase. This allows a comparison to be made between different models.

Corrections to the calculated liquidus temperatures for the effects of pressure and melt $H_2O$ contents are set in the 'Correction for models:' subsection of the Parameters Section of the Main form (Fig. 5.1) in the same way as for Crystallisation calculations (see sections **4.1.1.3 and 4.1.1.4**).

***Note:*** The same correction will apply to all models selected for a phase. If a selected model incorporates the effects of pressure and/or $H_2O$, then the option 'Apply $H_2O$ and P Corrections to All Models' (see Section 1.2) defines whether the correction(s) will apply to that model. When the option is selected, the correction(s) will apply to models that incorporate the effects of pressure and/or $H_2O$.

If the $H_2O$ and / or $CO_2$ contents in the starting composition(s) exceed fluid saturation values for the chosen pressure, their concentrations will be adjusted to match saturation at the chosen pressure *before temperatures are calculated*.

If the S content in the starting composition(s) exceeds sulphide or sulphate saturation, S concentrations will be adjusted to match saturation *before temperatures are calculated*.

***Note:*** If the starting composition is sulphide, sulphate, zircon, apatite or fluid saturated, the established liquidus temperature is assigned to these phases and used for calculating their compositions.

***Note:*** The oxidation states of Fe and S in the melt composition recorded in the results output correspond to the established liquidus temperature (i.e., the highest calculated temperature among the models chosen for calculation).

When models of Danyushevsky (2001) for olivine *AND* plagioclase are chosen, Petrolog4 automatically estimates the $H_2O$ content in the melt which is required for the starting composition to lie on an olivine + plagioclase cotectic. The estimated $H_2O$ content is reported for each composition below the line with mineral compositional parameters (Fig. 5.1).

When models of Danyushevsky (2001) for olivine *AND* clinopyroxene are chosen, Petrolog4 automatically estimates crystallisation pressure at which the starting composition has both olivine and clinopyroxene on its liquidus. The estimated crystallisation pressure is reported for each composition below the line with mineral compositional parameters (Fig. 5.1).

***Note:*** Models of Danyushevsky (2001) are calibrated for MORB and BABB compositions only and should not be used for calculations with compositions from other tectonic settings.

If the starting composition contains either $H_2O$ or $CO_2$ or both, Petrolog4 automatically estimates fluid saturation pressures for the starting composition using all available models of fluid saturation. The estimated fluid saturation pressure is reported for each composition below the line with mineral compositional parameters (Fig. 5.1).

***Note:*** If the starting composition is fluid-oversaturated relative to the pressure chosen for calculations, the saturation pressure will be calculated for the *unmodified* starting composition before its volatile contents are adjusted to reflect saturation at the pressure chosen for calculation. Since calculations of the saturation pressure involve melt liquidus temperature, it is recommended that the calculation pressure is set above the saturation pressure of the starting composition(s) to ensure that the calculated liquidus temperature is appropriate for the volatile contents of the starting composition.

Since crystallisation calculations are not performed under this Option, the number of calculation parameters that can be set by the user is significantly less compared to Crystallisation calculations.

Fluid, sulphur, apatite and zircon saturation models are set in the 'Saturation models:' subsection of the Parameters Section of the Main form (Fig. 5.1) in the same way as for Crystallisation calculations (see section **4.1.4**).

Melt oxidation state is set in the 'Oxidation state' subsection of the Parameters Section of the Main form (Fig. 5.1) in the same way as for Crystallisation calculations (see section **4.1.5**).

Pressure is set in the 'Pressure' subsection of the Parameters Section of the Main form (Fig. 5.1). It is possible to load pressure values to be used in calculations from the data file with analyses. That values can differ for each analysis (see **Section 4.1.3** for details).

***Note:*** If you would like to use additional options for calculating minerals compositions (see sections **4.1.1.1 and 4.1.1.2**), you should choose them in the Crystallisation tab as described in Section **4**.

### *5.1. Saving and loading calculation parameters and structure of output files*

Saving and Loading calculation parameters is done in the same way as for Crystallisation calculations (see section **4.2**).

During melt liquidus association calculations, Petrolog4 saves the following files:

FileName_MLA___calc_param.csv file lists values of all calculation parameters.

FileName_MLA__.csv file contains the starting melt composition, and pseudo-liquidus temperatures and compositional parameters of phases for the selected models.

***Note:*** When exporting results of previous calculations to Excel, the user ***must*** click on the FileName_MLA__.csv file to initiate export.

Compositions of each phase in equilibrium with the melt are saved in a separate file that have the same naming convention as for Crystallisation calculations (e.g., file FileName_MLA_Olv.csv contains olivine compositions).

***Note:*** When 'Add export of elemental concentrations to files' option is used (see Section 1.2), an additional set of files with phase compositions will be add that have '_EL' added at the end of their names (e.g., FileName_MLA__EL.csv, FileName_MLA_Plg_EL.csv, etc.).

***Note:*** When using user-defined file names, it is recommended to keep file names under 15 characters long, since the length of allowed names for individual sheets in Excel files is limited to 31 characters.

## 6. Reverse of fractional crystallisation

To model reverse of fractional crystallisation, choose ‘Reverse Crystallisation’ tab of the Main form (Fig. 6.1).

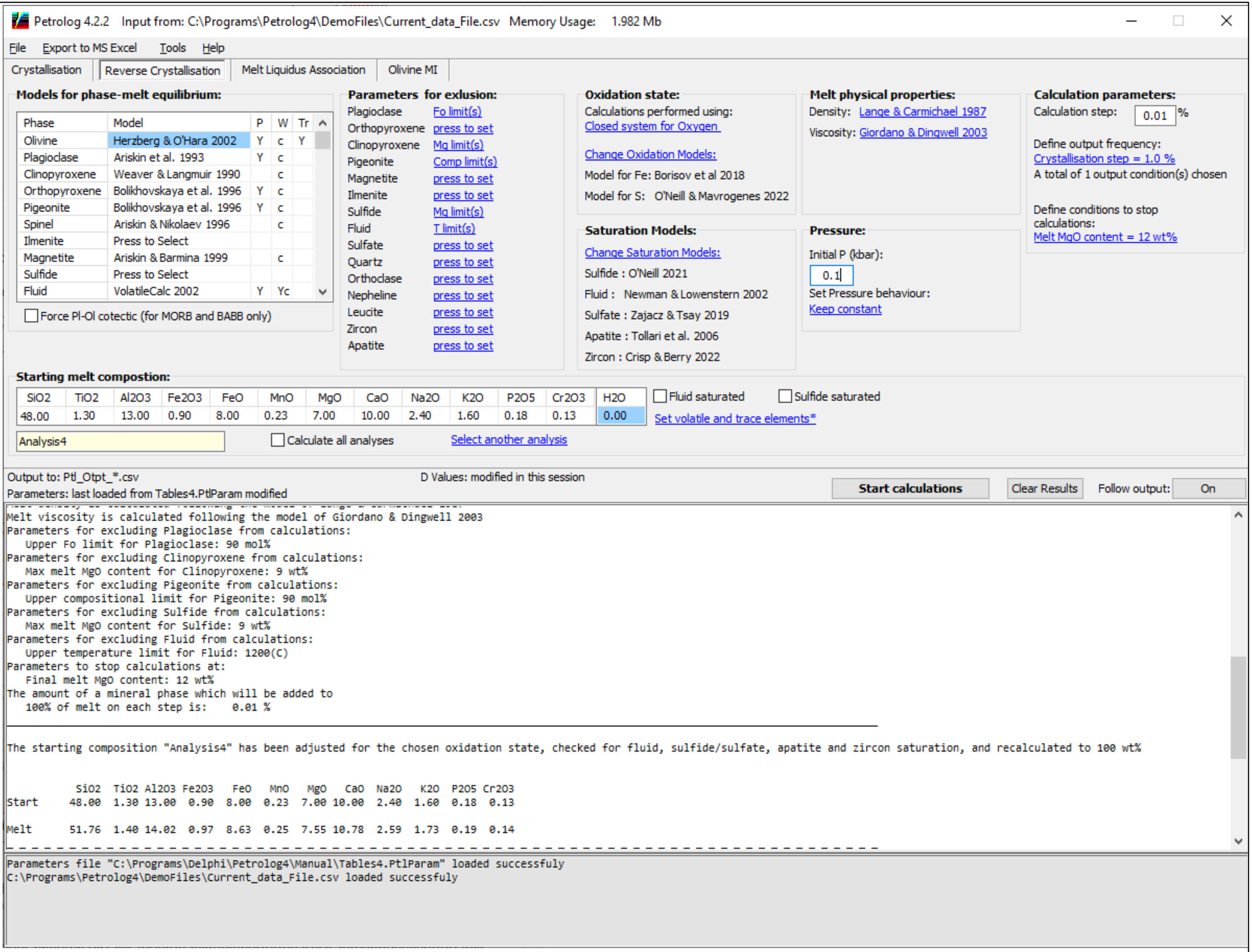



**Figure 6.1.** ‘Reverse crystallisation’ option of Petrolog4 interface.

***Note:*** It is recommended that you read Sections 4 and 5 of this manual before reading this section.

The algorithm for modelling the reverse of fractional crystallisation involves addition of phases that crystallized from the melt back to the melt composition thus moving it up along a cotectic (a liquid line of descent) towards more primitive compositions.

Unlike crystallisation calculations, where crystallisation of any number of phases can be modelled for any starting composition (as the algorithm determines which minerals crystallise from the melt), the phases that are included in the reverse of fractionation calculations *must* be on the liquidus of the starting composition at the chosen calculation parameters.

***Note:*** Phases that are present on the liquidus of the starting composition can be checked using the ‘Melt liquidus association’ option (see Section **3** of this manual).

Unlike crystallisation calculations, where the mineral with the highest pseudo-liquidus temperature is subtracted from the melt composition, the mineral with the lowest pseudo-liquidus temperature is added to the melt composition during reverse of fractionation calculations. The technique is least ambiguous when used with compositions that lie within a single-phase saturation field.

***Note:*** It is possible to calculate the reverse of pure fractional crystallisation only, as equilibrium crystallisation does not preserve sufficient information on the crystallisation history to enable reverse calculations.

Unlike crystallisation calculations, the algorithm for modelling the reverse of fractionation does not have a built-in mechanism for determining when minerals appeared on the liquidus during fractionation, and thus these conditions should be set by the user.

Consider an example with a melt composition having the following crystallisation sequence: first olivine, then plagioclase after 5% crystallisation (crystallisation along an olivine+plagioclase cotectic), and then clinopyroxene after 15% crystallisation (crystallisation along an olivine+plagioclase+clinopyroxene cotectic), with a total extent of crystallisation of 25%. Reversing this crystallisation sequence using the evolved melt composition formed after 25% of crystallisation would start with reversing crystallisation along the olivine+plagioclase+clinopyroxene cotectic. However, the algorithm cannot determine when clinopyroxene (or plagioclase) appeared on the liquidus during fractionation, and the timing of these events should be set by the user. Thus, the calculated trend of melt evolution is dependent on the conditions at which minerals are excluded from calculations to force the trend off a cotectic (refer to Danyushevsky and Plechov, 2011 for further explanations).

The parameters at which the melt moves off a given cotectic (i.e., parameters for phase exclusion) are set in the 'Parameters for Exclusion' subsection of the Parameters section of the Main form (Fig. 6.1). Click on the blue text label ('press to set') next to the desired mineral to open the 'Conditions for exclusion' pop-up window for this mineral (Fig. 6.2).

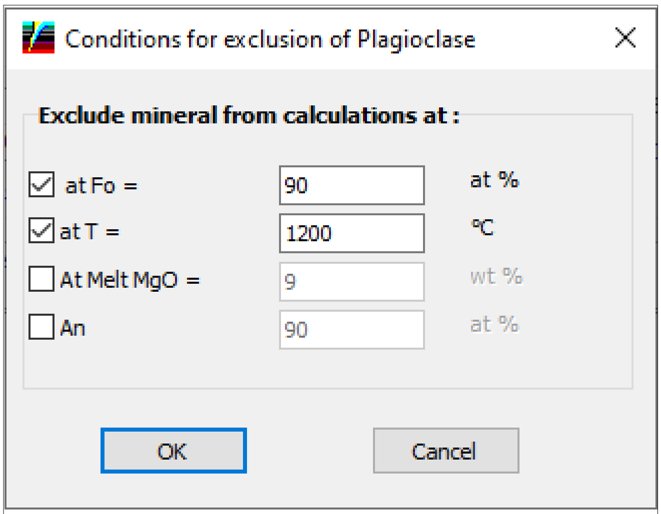



**Figure 6.2.** The 'Conditions for exclusion' window, showing four available options for specifying timing of plagioclase exclusion from calculations.

Petrolog4 offers four different options for setting the timing of exclusion for plagioclase and pyroxenes: 1) temperature; 2) melt MgO content; 3) composition of liquidus olivine; 4) the composition of the phase. For other phases the available options are temperature and melt MgO content. Several options can be set simultaneously, and the mineral will be excluded when one of the set conditions are met. Olivine and spinel cannot be excluded from calculations since primitive melts begin crystallising with olivine and spinel on their liquidus.

Close the window by pressing the 'Ok' button. Pressing the 'Cancel' button closes the window without applying the changes made. The blue label on the Main form will display the chosen option(s).

All other parameters for reverse of fractional crystallisation calculations are set in the same way as for Crystallisation calculation (see Section **4** of this manual).

***Note:*** The data file can contain columns that contain pressure to be used in calculations and conditions to stop calculations that can differ for each analysis. See section **4.1.10** for more details).

### *6.1. Saving and loading calculation parameters and structure of output files*

Saving and loading calculation parameters is done in the same way as for Crystallisation calculations (see section **4.2**).

During reverse of fractional crystallisation calculations, Petrolog4 saves the following files:
FileName_REV___calc_param.csv file lists values of all calculation parameters.
FileName_REV__.csv file contains the starting melt composition, and pseudo-liquidus temperatures and compositional parameters of phases for the selected models.

***Note:*** When exporting results of previous calculations to Excel, the user *must* click on the FileName_REV__.csv file to initiate export.

Compositions of each phase in equilibrium with the melt are saved in a separate file that have the same naming convention as for Crystallisation calculations (e.g., file FileName_REV_Olv.csv contains olivine compositions).

***Note:*** When ‘Add export of elemental concentrations to files’ option is used (see Section 1.2), an additional set of files with phase compositions will be add that have ‘_EL’ added at the end of their names (e.g., FileName_REV__EL.csv, FileName_REV_Plg_EL.csv, etc.).

***Note:*** When using user-defined file names, it is recommended to keep file names under 15 characters long, since the length of allowed names for individual sheets in Excel files is limited to 31 characters.

# 7. Modelling post-entrapment re-equilibration of melt inclusions in olivine

To model post-entrapment re-equilibration of melt inclusions in olivine, chose ‘Olivine MI’ tab of the Main form (Fig. 7.1).

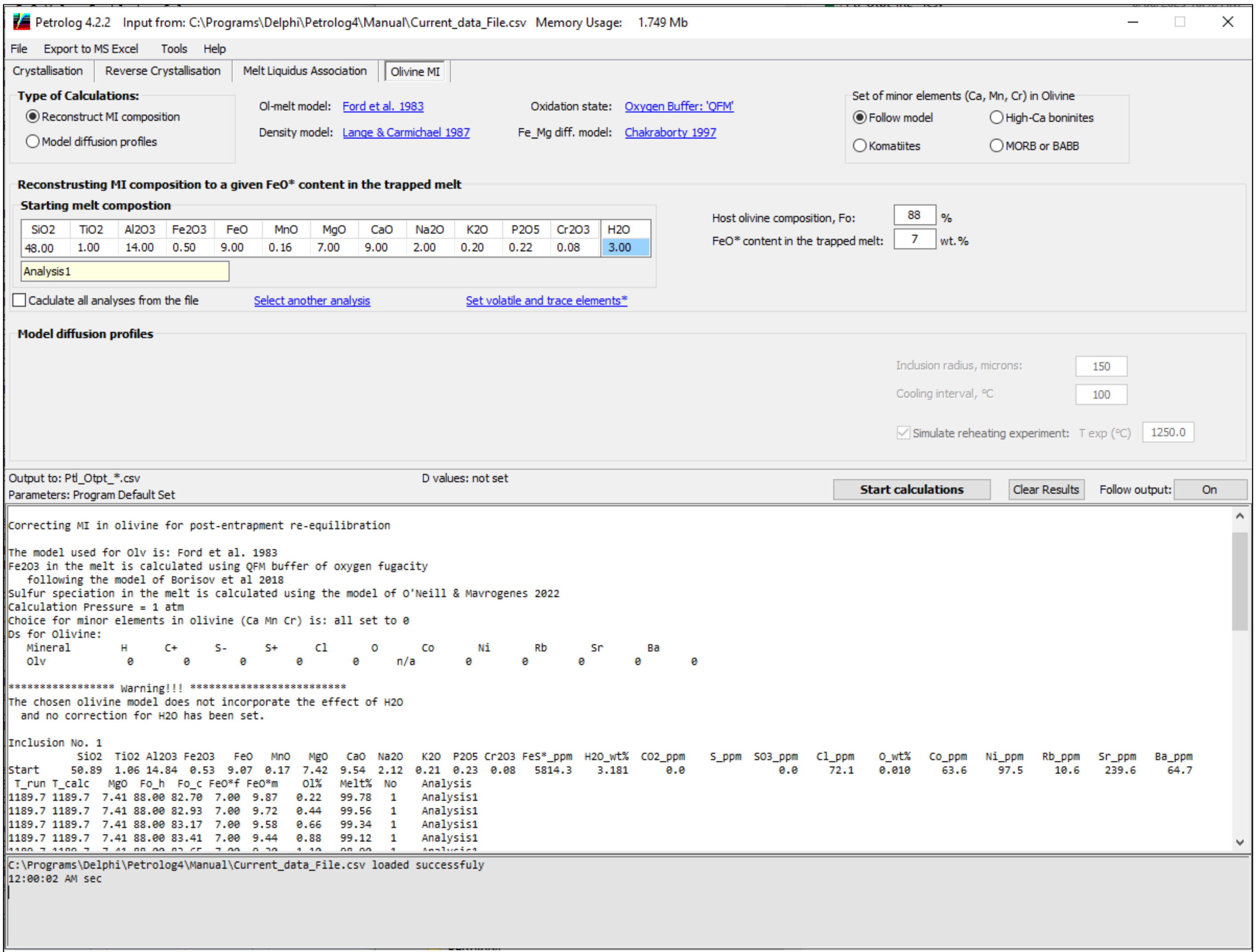



**Figure 7.1.** ‘Olivine MI’ option of Petrolog4 interface for reconstructing melt inclusion compositions.

***Note:*** It is recommended to read Sections 4, 5 and 6 of this manual before reading this section.

## *7.1. Reconstructing the initial trapped composition of the MI*

Re-equilibration of Fe and Mg between melt inclusions and their host olivine phenocrysts is described in detail by Danyushevsky *et al.* (2000a, 2002), with the main points summarised briefly below. The underlying assumption in these considerations is that the composition of the host olivine does not change after trapping of the melt inclusion.

Cooling of an inclusion after trapping results in crystallisation of olivine from the trapped melt, forming an olivine rim on the walls of the inclusion. The crystallising olivine rim is progressively enriched in Fe and depleted in Mg, i.e., becomes poorer in forsterite component, resulting in a compositional gradient within the rim. The existence of this compositional gradient causes re-equilibration of the inclusion with its host. This re-equilibration is achieved by diffusion of Fe out of, and Mg into the initial volume of the inclusion. This leads to a rapid decrease in Fe content of the residual melt inside the inclusion, a process referred to as ‘Fe-loss’ by Danyushevsky *et al.* (2000a).

Conversely, if an olivine grain containing a melt inclusion is heated over the temperature of inclusion entrapment, host olivine around the inclusion would melt, increasing the Mg# of the melt inside the inclusion and resulting in disequilibrium between the melt and host olivine. This leads to re-equilibration of the melt with the host, which is achieved by diffusion of Fe into, and Mg out of the melt inside the inclusion. This leads to a rapid increase in Fe content of the melt, a process that can be referred to as 'Fe-gain'.

Petrolog4 offers an option of reconstructing the initially trapped melt composition, providing that the user specifies the FeO* content of the trapped melt. The algorithm simulates the following experimental procedure:

**I**. An olivine grain containing an inclusion is kept at a given temperature until the inclusion is in complete equilibrium with the host. Within the algorithm, this temperature corresponds to the olivine liquidus temperature of the melt inclusion composition provided (the starting melt composition). The algorithm simulates exchange of Fe and Mg between melt and olivine, which occurs during the re-equilibration process. Re-equilibration may be accompanied by either melting or crystallisation of the host olivine at the inclusion walls.

**II**. Once equilibrium is reached, the algorithm compares the FeO* content of the melt with the user-specified FeO* content of the trapped melt.

**III**. If the user-specified FeO* content is higher than the FeO* content of the melt, the algorithm simulates increasing experimental temperature while keeping the melt inclusion and its host in equilibrium. If the user-specified FeO* content is lower than the FeO* content of the melt, the algorithm simulates decreasing experimental temperature while keeping the melt inclusion and its host in equilibrium. In both cases this continues until the FeO* content within the melt inclusion equals the user-specified value. The algorithm simulates melting or crystallisation of olivine and the exchange of Fe and Mg between melt and olivine, which occur during this process.

To use this option, click on the 'Reconstruct MI composition' radio button in the 'Type of Calculations' subsection of the Parameters section of the Main form (Fig. 7.1).

The user must provide the composition of the melt inside the inclusion, the composition of the host olivine (Fo, mol%), and the FeO* content of the trapped melt. These parameters are set within the 'Reconstructing MI composition to a given FeO* content of the trapped melt' subsection of the Parameters section of the Main form (Fig. 7.1).

***Note:*** If you would like to load data from a file and use the 'Calculate all analyses from the file' option, the data file must include columns that contain the host olivine composition and the FeO* content of the trapped melt for each analysis, The column names for these two parameters should read 'Fo_h' or 'Fo_fost'. and 'FeO_final' or 'FeO_fin' or 'FeO_rock', respectively (not case sensitive).

User-specified calculation parameters for this option include: olivine-melt equilibrium model; melt oxidation state, model for calculating melt density, and a model for calculating minor element contents (Ca, Mn, Cr) in olivine. The first three parameters are set in the same way as described in Section **4** of this manual. The last parameter allows the user to introduce minor elements into the calculated olivine composition. The contents of these elements are calculated as a function of olivine Fo content, and are set to typical values for either komatiites, or high-Ca boninites, or MORB / BABB. If the contents of these elements in olivine are set to 0 (None), they are modelled as perfectly incompatible elements.

***Note:*** All calculations within this option are performed at a pressure of 1 atm.

During calculations, Petrolog4 records intermediate output in the Output section of the Main form. This output is provided mainly to keep the user informed of the progress of calculations. Petrolog4 writes the results of calculations into output files.

***Note:*** The reconstructed inclusion composition is automatically copied in the 'Model diffusion profiles' subsection of the Parameters section to be used in modelling diffusion profiles if required.

### 7.1.1. Saving and loading calculation parameters and structure of output files

Saving and loading calculation parameters is done in the same way as for Crystallisation calculations (see Section **4.2**).

During reconstructing melt inclusion composition calculations, Petrolog4 saves the following files:

FileName_IRL___calc_param.csv file lists values of all calculation parameters.

FileName_IRS__.csv file contains the main output.

For each inclusion, Petrolog4 writes three lines into the output file. The first line, marked by value '1' in the 'No.' column, corresponds to the starting composition. The second line, marked by value '2' in the 'No.' column, corresponds to the moment when inclusion reaches equilibrium with the host (end of step I above). The third line, marked by value '3' in the 'No.' column, corresponds to the result of the calculations, when inclusion is in equilibrium with the host and the FeO* in the melt matches the user-defined value.

Values in the 'CORR_COEF' column in the output file should be used to calculate the weight concentrations of perfectly incompatible elements in the recalculated inclusion compositions, by multiplying the values in the starting composition by this coefficient. The values in the 'OL_PER' and 'MELT_PER' columns show weight fractions of olivine and the starting melt during calculations (negative values in the 'OL_PER' column indicate melting of olivine from the walls). These values do not represent the final weight percent change to the starting composition, as inclusions are modelled as open systems to allow for Fe/Mg inter-diffusion during calculations.

***Note:*** When exporting results of previous calculations to Excel, the user *must* click on the FileName_IRL__.csv file to initiate export.

### *7.2. Modelling diffusive re-equilibration during 'Fe-loss'*

Known values of the diffusion coefficient for Fe-Mg inter-diffusion ($D_{Fe\text{-}Mg}$) in olivine allow calculation of the time required for re-equilibration to occur. If an inclusion is completely re-equilibrated, it is possible to calculate the minimum time that the host phenocryst spent at temperatures between trapping and diffusion closure. However, if re-equilibration is not complete when the closure temperature is reached, and thus a diffusion profile around the inclusion is preserved, a quantitative time estimate can be made.

***Note:*** This technique does not allow an estimate of the residence time at (or close to) the trapping temperature, since at these conditions there is no (or very little) crystallisation within the inclusion.

Petrolog4 uses the data from Chakraborty (1997) to calculate the value of $D_{Fe\text{-}Mg}$:
Lg(D_FeMg) = -10757/T(K) - 9.9453+ 0.8063/Fo, in sec/$m^2$, where Fo is (Mg/(Fe+Mg)) in olivine.

Petrolog4 offers an option for forward modelling of the re-equilibration process during cooling after entrapment (i.e., for the case of 'Fe-loss'). To choose this option, press the 'Model diffusion profile' radio button in the 'Type of Calculations' subsection of the Parameters section of the Main form (Fig. 7.2).

The user must provide the trapped inclusion composition, the inclusion radius (microns) and the length of the cooling interval (in $^{o}$C). These parameters are set within the 'Model diffusion profiles' subsection of the Parameters section of the Main form (Fig. 7.2).

***Note:*** In this option, the starting composition cannot be imported from a data file.

User-specified calculation parameters for this option include: olivine-melt equilibrium model; melt oxidation state, model for calculating melt density, Fe-Mg inter-exchange diffusion model, and a model for calculating minor element contents (Ca, Mn, Cr) in olivine. The first three parameters are set in the exactly the same way as described in Section **2** of this manual. The last parameter allows the user to introduce minor elements into the calculated olivine composition. The contents of these elements are calculated as a function of olivine Fo content, and are set to typical values for either komatiites, or high-Ca boninites, or MORB / BABB. If the contents of these elements in olivine are set to 0, they are modelled as perfectly incompatible elements.

***Note:*** All calculations within this option are performed at a pressure of 1 atm.

Diffusion modelling can be performed either for the case of instant cooling, or for the case of cooling with a specific cooling rate.

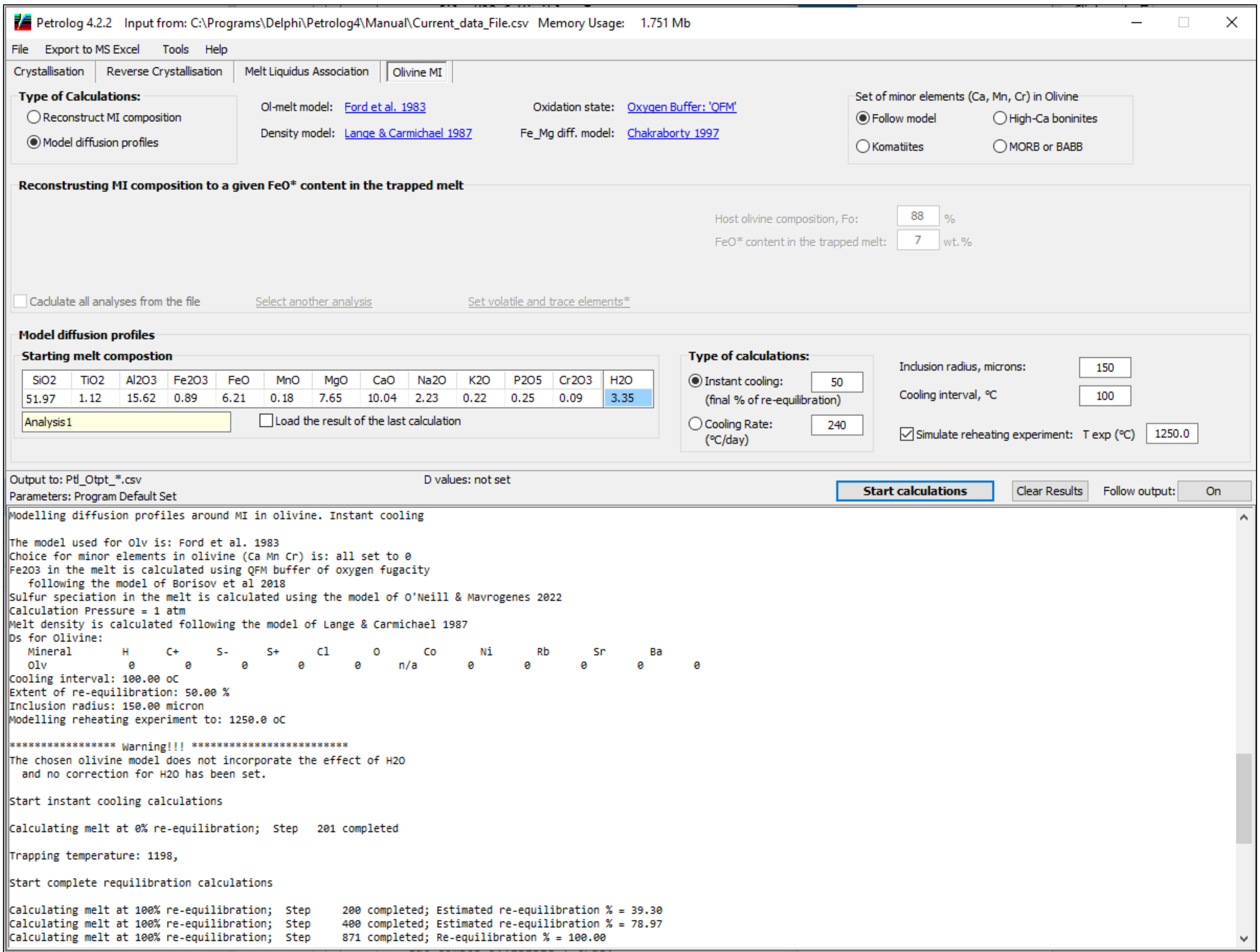



**Figure 7.2.** 'Olivine MI' option of Petrolog4 interface for modelling diffusion profiles around melt inclusions. Note that the Debug Section at the bottom of the Main Form is not displayed on this example as Debug output has been switched off by using the 'DebugOutput On/Off' item in the 'Tools' section of the Main Menu.

### 7.2.1. Instant cooling calculations

In the case of instant cooling, the zoned rim on the walls of the inclusion grows first and then re-equilibration occurs while the grain resides at the lower end of the cooling interval. To use this option, click on the 'Instant cooling' radio button in the 'Type of calculations' subsection within the 'Model diffusion profiles' subsection in the Parameters section of the Main form (Fig. 7.2). For this option, the user needs to specify the extent of re-equilibration, a parameter that will be used to determine when diffusion calculations are completed. This parameter is set in the text box next to the 'Instant cooling' radio button. The degree of re-equilibration, i.e., the extent of 'Fe-loss', is defined as the amount of FeO* 'lost' by the residual melt relative to the amount that is 'lost' in the case of complete re-equilibration.

The output file generated within this option contains the melt compositions and diffusion profiles generated at different stages of calculations. The diffusion profiles are expressed as values of FeO* concentration in olivine over distance from the centre of the melt inclusion. The melt compositions recorded correspond to: 1) the starting composition, 2) the composition of the melt after instant cooling (0% re-equilibration), the composition of the melt in the case of complete re-equilibration (100%), and the composition of the melt at the required extent of re-equilibration. The FeO* profiles recorded correspond to the initial rim profile after the instant cooling, and to the resultant FeO* profile after the calculations are completed.

### 7.2.2. Cooling rate calculations

In the case of cooling with a specific cooling rate, re-equilibration and cooling occur simultaneously. To use this option, click on the 'Cooling Rate' radio button in the 'Type of calculations' subsection within the

‘Model diffusion profiles’ subsection in the Parameters section of the Main form (Fig. 7.2). For this option, the user needs to specify the cooling rate, and the calculations will simulate cooling with the specified rate from the start to the end of the cooling interval. This parameter is set in the text box next to the ‘Cooling Rate’ radio button.

Modelling of diffusion under this option is performed in 10 $^{o}$C steps, with each step modelled as a separate instant cooling calculation. The program generates two output files. One file contains a record of diffusion profiles at the end of each 10-degree step, and the second file contains melt compositions at the end of each step. ‘PR’ at the end of the file name denotes files containing calculated FeO profiles. ‘COMP’ at the end of the file name denotes files containing calculated melt compositions.

### 7.2.3. Modelling complex cooling histories

To enable modelling of complex cooling histories, Petrolog4 allows for using the result of the last calculation as the starting point for the next calculation. For this purpose, after each diffusion modelling calculation Petrolog4 saves both the final profile and the final melt composition into a file called ‘LAST_RES.DAT’. In order to use the results of the last calculation as the starting point for the following calculation, check the ‘Load last result’ checkbox in the ‘Diffusion profiles modelling’ part of the Parameters section of the Main form (Fig. 4.16).

***Note:*** Loading the results of the last calculation automatically sets the size for the inclusion radius, which should not be changed.

***Note:*** It is recommended that the user does not delete file ‘LAST_RES.DAT’ from the directory which contains the Petrolog4 executable (i.e., ‘Petrolog.exe’ file).

### 7.2.4. Simulating reheating experiments

Calculation under both Instant cooling and Cooling rate options can simulate a reheating experiment with the melt inclusions, an optional calculation performed at the end of diffusions modelling. To include this calculation, check the ‘Simulate reheating experiment’ checkbox within the ‘Model diffusion profiles’ subsection in the Parameters section of the Main form (Fig. 7.2). The user is then also required to provide a temperature value for the reheating experiment. The temperature is set in the ‘T exp (°C)’ text box next to the ‘Simulate reheating experiment’ checkbox.

Using this option allows Petrolog4 to reproduce the following scenario: 1) inclusion is trapped; 2) after entrapment, inclusion is cooled within the plumbing system prior to eruption; 3) the grain with the inclusion is experimentally reheated to a certain temperature and quenched. The results of diffusion modelling can then be directly compared with the analysed composition of the experimentally quenched inclusion.

***Note:*** If the results of a diffusion modelling calculation are intended to be used in the following calculation, simulation of the reheating experiment should not be performed.

### 7.2.5. Integrating reconstruction of inclusion compositions and diffusion modelling

To facilitate combining calculations of the initial trapped inclusion compositions with diffusion modelling, Petrolog4 populates the Starting melt composition for the ‘Model diffusion profiles’ option with the result of the calculation performed with the ‘Reconstructing MI composition to a given FeO* value’ option. Temperature value for experimental reheating is also set to correspond to the olivine liquidus temperature of the starting composition for the ‘Reconstructing MI composition to a given FeO* content in the trapped melt’.

***Note:*** It is recommended that the user contacts Petrolog4 support if advanced use of the diffusion modelling is intended.

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## Appendix 1. List of available models and other technical information

***Olivine-melt equilibrium models:*** Ariskin et al., 1986; Ariskin et al., 1993; Beattie, 1993; Bychkov, 2023; Danyushevsky, 2001; Ford et al., 1983; Gaetani and Watson, 2002; Herzberg and O'Hara, 2002; Langmuir et al., 1992; Nathan and Vankirk. 1978; Nielsen, 1985; Nielsen, 1988; Putirka, 2005; Roeder and Emslie, 1970; Sobolev and Slutskiy, 1984; Weaver and Langmuir, 1990.

***Olivine-melt Fe-Mg exchange Kd models*:** Kd = const'; 'Ln(Kd) = A/T(K)+B*P(kbar)/T(K)+C'; Sobolev and Danyushevsky, 1994; Toplis, 2005.

***Plagioclase-melt equilibrium models**:* Ariskin and Barmina, 1990; Ariskin et al., 1993; Bychkov, 2023; Danyushevsky, 2001; Drake, 1976; Langmuir et al., 1992; Nathan and Vankirk. 1978; Nielsen, 1985; Nielsen and Dungan, 1983; Plechov and Gerya, 1998; Weaver and Langmuir, 1990.

***Clinopyroxene-melt equilibrium models:*** Ariskin et al., 1986; Ariskin et al., 1993; Bychkov, 2023; Danyushevsky, 2001; Langmuir et al., 1992; Nathan and Vankirk. 1978; Nielsen, 1985; Nielsen, 1988; Nielsen and Drake, 1979; Weaver and Langmuir, 1990.

***Orthopyroxene-melt equilibrium models:*** Ariskin et al., 1993; Beattie, 1993; Bolikhovskaya et al., 1995; Bychkov, 2023; Nathan and Vankirk. 1978; Nielsen and Drake, 1979.

***Pigeonite-melt equilibrium models*:** Ariskin et al., 1986; Ariskin et al., 1993; Bolikhovskaya et al., 1995; Bychkov, 2023; Nielsen, 1988.

***Spinel-melt equilibrium models:*** Ariskin and Nikolaev, 1996; Nielsen, 1985.

***Ilmenite-melt equilibrium models:*** Ariskin and Barmina, 1999; Nielsen, 1985.

***Magnetite-melt equilibrium models:*** Ariskin and Barmina, 1999; Nathan and Vankirk. 1978.

***Quartz-melt equilibrium models:*** Nathan and Vankirk. 1978; Plechov et al., 2023.

***Orthoclase-melt equilibrium models:*** Nathan and Vankirk. 1978.

***Nepheline-melt equilibrium models:*** Nathan and Vankirk. 1978.

***Leucite-melt equilibrium models:*** Nathan and Vankirk. 1978.

***Sulphide melt- silicate melt equilibrium models:*** Kiseeva and Wood, 2015; O'Neill, 2021; pure FeS.

***Sulphate melt- silicate melt equilibrium models:*** pure anhydride $CaSO_4$).

***Fluid-melt equilibrium models:*** Iacono-Marziano et al, 2012; Newman and Lowenstern, 2002 (VolatileCalc); pure H2O; pure CO2.

***Zircon-melt equilibrium models:*** pure zircon ($ZrSiO_4$).

***Models for setting $H_2O$ corrections to calculated temperatures:***

*Olivine:* Almeev et al., 2007; Danyushevsky, 2001; Medard and Grove, 2008.

*Plagioclase:* Almeev et al., 2012; Danyushevsky, 2001.

*Orthpyroxene:* Koch et al., 2025.

***Sulphide saturation models:*** Ding et al., 2018; Fortin et al., 2015; Li and Ripley, 2005; Li and Ripley, 2009; O'Neill, 2021; Smythe et al., 2017; Wallace and Carmichael, 1992.

***Sulphate saturation models:*** Zajacz and Tsay, 2019.

***Fluid saturation models:*** Iacono-Marziano et al., 2012; Moore et al., 1998; Newman and Lowenstern, 2002, Shishkina et al., 2014.

***Apatite saturation models:*** Tollari et al., 2006.

***Zircon saturation models:*** Borisov et al., 2025; Crisp and Berry, 2022.

***Models of Fe oxidation state in the melt:*** Borisov and Shapkin, 1990; Borisov et al., 2018; Kilinc et al., 1983; Kress and Carmichael, 1988; Kress and Carmichael, 1991; Sack et al., 1980.

***Models of S oxidation state in the melt:*** Boulliung and Wood, 2023; Jugo, 2009; Nash et al., 2019; O'Neill and Mavrogenes, 2022.

***Melt density models:*** Lange and Carmichael, 1997; Nelson and Carmichael, 1979

***Melt viscosity models:*** Bottinga and Weill, 1972 and Giordano and Dingwell, 2003.

***Models for trace element distribution coefficients between a phase and the silicate melt:***
*Olivine:* Beattie et al., 1991 (Ni and Co); Kinzler et al., 1990 (Ni); Koshlyakova et al., 2022 (Ni);
*Plagioclase:* Blundy and Wood, 1991 (Ba and Sr)
*Clinopyroxene:* Wood and Blundy, 1997 (Y and REE)
*Fluid:* Ding et al., 2023 ($S^{2-}$ and $S^{6+}$).

***Petrolog4 default corrections to the calculated pseudo-liquidus temperature for the effect of melt H2O content***: The corrections are power functions dT ($^oC$) = A * ($H_2O$ wt.%)$^B$ with the following coefficients:

| | | |
|---|---|---|
| *Feldspars and Quartz*: | A = 121.75 | B = 0.512; |
| *Orthopyroxene*: | A = 100.0 | B = 0.45; |
| *Clinopyroxenes*: | A = 90.0 | B = 0.37; |
| *Olivine, Oxides and Feldspathoids*: | A = 74.404 | B = 0.352. |

***Petrolog4 default corrections to the calculated pseudo-liquidus temperature for the effect of pressure***:
The corrections are linear functions with the following slopes:

| | |
|---|---|
| *Pyroxenes*: | 10 $^o$/kbar; |
| *All other minerals*: | 5 $^o$/kbar. |

***Oxygen buffers:***
Buffer equations are from Iacovino (2022) based on Frost (1991).

| **Lg $fO_2$ = A / TK + B + C * ($P_{bar}$-1) / TK** | | | |
|---|---|---|---|
| **Buffer** | **A** | **B** | **C** |
| QFFe | -29520.8 | 7.492 | 0.05 |
| Fe-W | -27489 | 6.702 | 0.055 |
| WM | -32807 | 13.012 | 0.083 |
| Co-CoO | -24332.6 | 7.295 | 0.052 |
| QFM | -25096.3 | 8.735 | 0.11 |
| Ni-NiO | -24930 | 9.36 | 0.046 |
| MH | -25700.6 | 14.558 | 0.019 |

***Atomic weights (amu) and charges*** *(all atomic weights from https://iupac.qmul.ac.uk/AtWt/ "ATOMIC WEIGHTS OF THE ELEMENTS 2021" ;   * S+ has a charge of +4 in fluid)**:***

| | **Si** | **Ti** | **Al** | **Fe3** | **Fe2** | **Mn** | **Mg** | **Ca** | **Na** | **K** | **P** | **Cr** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Atomic wt. | 28.09 | 47.88 | 26.98 | 55.85 | 55.85 | 54.94 | 24.31 | 40.08 | 22.99 | 39.1 | 30.97 | 52 |
| Charge | 4 | 4 | 3 | 3 | 2 | 2 | 2 | 2 | 1 | 1 | 5 | 3 |

| | **H** | **C+** | **S-** | **S+** | **Cl** | **O** | **Li** | **B** | **Be** | **Sc** | **V** | **Co** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Atomic wt. | 1 | 12.01 | 32.06 | 32.06 | 35.45 | 16 | 6.94 | 10.81 | 9.01 | 44.96 | 50.94 | 58.93 |
| Charge | 1 | 4 | -2 | 6 * | 0 | -2 | 1 | 3 | 2 | 3 | 3 | 2 |

| | **Ni** | **Cu** | **Zn** | **Ga** | **Rb** | **Sr** | **Y** | **Zr** | **Nb** | **Ru** | **Rd** | **Pd** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Atomic wt. | 58.69 | 63.55 | 65.39 | 69.72 | 85.47 | 87.62 | 88.91 | 91.22 | 92.91 | 101.1 | 102.9 | 106.4 |
| Charge | 2 | 1 | 2 | 3 | 1 | 2 | 3 | 4 | 5 | 4 | 4 | 4 |

| | Cs | Ba | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Atomic wt. | 132.9 | 137.3 | 138.9 | 140.1 | 140.9 | 144.2 | 150.4 | 152 | 157.2 | 158.93 | 162.5 | 164.9 |
| Charge | 1 | 2 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |

| | Er | Tm | Yb | Lu | Hf | Ta | Re | Os | Ir | Pt | Pb | Th | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Atomic wt. | 167.3 | 168.9 | 173 | 175 | 178.5 | 180.9 | 186.2 | 190.2 | 192.2 | 195.1 | 207.2 | 232 | 238 |
| Charge | 3 | 3 | 3 | 3 | 4 | 5 | 4 | 4 | 4 | 4 | 2 | 4 | 4 |

***Redox equilibria:***

$FeS_{\_melt} + 8*FeO_{1.5\_melt} = SO_{3\_melt} + 9*FeO_{\_melt}$

$SO_{3\_melt} + 2*FeO_{\_melt} = SO_{2\_fluid} + 2*FeO_{1.5\_melt}$